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LIGHT - CATALYZED CHLORINE OXIDATION
FOR
TREATMENT OF WASTEWATER

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27 Abstract
A small scale batch reactor and a larger scale batch-recycle reactor were used to determine optimum illumination and chlorine dose for oxidation of the soluble organics in secondary waste water effluent. Primary variables studied included wavelength effects, intensity-time relationships, quantum efficiencies, chlorine concentration, and the effect of dissolved oxygen. For optimal operation, light of low intensity and less than 300 wavelength, and chlorine of less than 5 mg/l should be used. Process cost estimates were made for a 10 mgd plant. Initial investments were estimated at $990,000. Fixed charges were estimated at 3.42¢/1000 gal, and operating costs were figured as: (1) labor-2.79¢/1000 gal; (2) lamp replacement-1.70¢/1000 gal, and (3) chlorine 2.09¢/1000 gal. With an additional 1.77¢/1000 gal for miscellaneous expenses, total operating costs were 8.35¢.1000 gal. Major assumptions used for cost estimation were: (1) 15 mg/l COD decrease required; (2) 1.30 quantum efficiency; (3) a stoichiometric amount of chlorine, and (4) continuous addition of caustic. Estimated overall costs were 11.77¢/1000 gals. Further cost decreases may occur as the result of developments in: (1) more intense and/or more efficient lighting; (2) utilization of higher quantum efficiencies due to improved operating conditions, and (3) ways of reducing the dosages of chlorine and caustic required. (Lowry-Texas)

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LIGHT-CATALYZED CHLORINE OXIDATION FOR TREATMENT OF WASTEWATER

by

Midwest Research Institute
Kansas City, Missouri 64110

for the

WATER QUALITY OFFICE

ENVIRONMENTAL PROTECTION AGENCY

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ABSTRACT

The purpose of this research effort was to determine the feasibility of applying the light-catalyzed chlorine oxidation process to the treatment of effluents from secondary waste-treatment plants.

(a) Studies were made of wavelength effects and intensity-time effects for the purpose of selecting the most practical source of radiant energy for the process.

(b) A batch-recycle reactor was constructed to establish certain plant-design parameters for low-pressure mercury arcs under conditions which simulated large-scale operations.

(c) Cost estimates were made for the application of this process to a plant producing 10 million gallons of effluents per day.

The wavelength-effect studies, mentioned in (a), indicated that short-wavelength radiation (below 300 mμ) is more effective than long-wavelength radiation in promoting the chlorine oxidation process. Analysis of the wavelength-effect experiments indicated that mercury-arc lamps are the most practical sources of radiant energy for this process. However, the ideal mercury-arc lamp is probably not commercially available. Of presently available sources, low-pressure mercury arcs are probably the most practical.

The intensity-time studies, mentioned in (a), indicated that the rate of organic oxidation, achieved in a given irradiation time, is increased by increased radiation intensity; however, for a specified amount of absorbed radiant energy, lower intensities produce more overall organic oxidation than do higher intensities. These studies also established that the chlorine consumption is directly proportional to the amount of radiant energy absorbed, regardless of intensity.

Experiments with the batch-recycle reactor, mentioned in (b), provided data for the precise determination of the quantum efficiency which is defined as the amount of organic oxidation obtained from a given amount of absorbed radiant energy. Higher quantum efficiencies were observed at low intensities, and the quantum efficiency increased as the oxidation proceeded.

Increases in chlorine concentration above 5 mg/liter produced no significant increase in the oxidation rate; increased chlorine concentrations, however, resulted in inefficient utilization of chlorine and radiant energy.

Thus, for optimum organic oxidation rate, optimum utilization of radiant energy and most efficient use of chlorine, (1) low-intensity short-wavelength radiation should be employed, and (2) the chlorine concentration should be at a minimum. The optimum chlorine concentration has not been established, but it is probably below 5 mg/liter.

In the presence of relatively large amounts of chlorine, oxygen has no significant effect on either the rate or the extent of oxidation. Under the experimental conditions investigated, it was not possible to detect whether or not any oxygen had participated in the organic oxidation.

A large-scale tertiary-treatment plant was designed to utilize commercially available, low-pressure, mercury-arc lamps. The reactor design allowed for long contact time (40 min) and low-intensity radiation. In the design, the lamps were spaced in the reactor in such a manner that practically all of the available radiation would be absorbed. Also, the spacing of the lamps allowed for the decrease in absorption as the reaction proceeded.

Process-cost estimates, mentioned in (c), were based on a 10-million gal./day plant representing an investment of $990,000. Fixed charges based on this investment were estimated at 3.42¢/1,000 gal. Operating costs of 8.35¢/1,000 gal. were estimated, of which the major costs were: labor, 2.79¢/1,000 gal.; lamp replacement, 1.70¢/1,000 gal.; and chlorine, 2.09¢/1,000 gal. Major assumptions were based on experimental results and were as follows: (1) a required COD decrease of 15 mg/liter, (2) a quantum efficiency of 1.30, (3) a stoichiometric amount of chlorine, and (4) a continuous addition of caustic.

The estimated overall costs of 11.77¢/1,000 gal. could be reduced significantly by: (1) the development of more intense and/or more efficient mercury-arc lamps, (2) the selection of operating conditions which would permit higher quantum efficiencies, or (3) the requirement of lesser amounts of chlorine or caustic.

This report was submitted in fulfillment of Project Number 17020DUE, Contract 14-12-531, under the sponsorship of the Water Quality Office, Environmental Protection Agency.

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RECOMMENDATIONS

An examination of process-cost estimations indicates that three major factors must be evaluated before an accurate determination can be made of the cost of applying the UV-chlorine process to secondary effluents. These factors are: (1) the conditions which will give maximum quantum efficiency, (2) the minimum amounts of chlorine and caustic that are required, and (3) the relative utility of radiant energy sources which produce higher intensities.

The quantum efficiency is a measure of the amount of radiant energy required to produce a specified amount of oxidation. Higher quantum efficiencies would permit significantly lower operating and plant-investment costs. Experiments to date indicate that quantum efficiencies much higher than those used in the process-cost estimates may be feasible.

Significant reductions in cost would also be possible if less chlorine and caustic were required. Preliminary experiments indicate that such reductions might be feasible.

A further significant reduction in plant-investment cost would be possible if higher intensity, radiant-energy sources could be used. Higher intensities permit smaller and less expensive reactors, but higher intensities also result in lower quantum efficiencies. There is a great difference between the relative intensities of the two types of commercially available, mercury-arc lamps. Experimental determination must be made of the relative advantages of each kind of lamp.

Studies designed to investigate maximum quantum efficiency should consist of: (1) an examination of lower radiation intensities than previously studied, and (2) a determination of the minimum chlorine concentration required to provide the maximum oxidation rate. These studies should include a determination of the relative effectiveness of radiation absorbed both by chlorine and by effluent at all stages of the oxidation.

The recommended study of minimum chlorine and caustic requirements should also involve relatively low chlorine concentration (perhaps 1 mg/liter or less). Although the most rapid rate of oxidation and the most efficient use of chlorine are obtained at pH 5, the most economical operation may be at ambient pH values, with little or no addition of caustic. The effect of oxygen on the rate and extent of oxidation under these conditions should be examined since oxygen may participate in the organic oxidation.

Finally, actual comparison experiments should be performed, using high- and low-pressure mercury arcs. The effectiveness of radiation from these lamps throughout the reaction zone should be determined by laboratory experiments in which the intensity of these lamps is varied. From these data, the overall rate and extent of the oxidation could be calculated at any point in the irradiated zone of the proposed, large-scale reactor.

A proposal (MRI Proposal No. C-2837, Revised) incorporating most of these studies has been submitted to the Federal Water Quality Administration.

INTRODUCTION

Earlier studies at Midwest Research Institute demonstrated the technical feasibility of employing chlorine and ultraviolet radiation for the elimination of dissolved organic material in highly nitrified effluents from biological, sewage-treatment plants. ("An Investigation of Light-Catalyzed Chlorine Oxidation for Treatment of Wastewater, Final Summary Report," FWPCA Contract No. 14-12-72, December 1968.) Chlorine will slowly oxidize only a small fraction of this organic material in the dark, but in the presence of ultraviolet radiation, rapid elimination of large amounts of COD and TOC is possible.

The purpose of the present work has been to provide additional information required for large-scale application of the process.

The body of this report consists of five major parts and an Experimental section: (1) The first major part describes wavelength-effect studies undertaken to determine the most practical source of radiant energy. (2) The second major part describes intensity-time studies undertaken to establish the relationship of these two important variables. (3) the third major part describes a series of experiments performed using a batch-recycle reactor. A reactor of this kind was very useful in determining certain plant-design parameters under conditions which simulated large-scale operation. (4) The fourth major part describes the effect of dissolved oxygen on the UV-chlorine oxidation when relatively large concentrations of chlorine are present. (5) The fifth major part is a review of process cost estimates.

There are two appendices to this report: Appendix A outlines the problems involved in selecting the most practical ultraviolet source for large-scale application of this process; Appendix B is a discussion of the problems encountered in selecting the techniques and equipment that were used in the wavelength-effect studies.

WAVELENGTH-EFFECT STUDIES

The most important factor in determining the feasibility of the light-catalyzed chlorine oxidation process for wastewater treatment is the selection of the most useful source of radiant energy from among the wide variety of types available. No prior information was available concerning the kind of radiant energy most effective in producing the desired reaction. On the other hand, many other chlorine reactions--for example, hydrocarbon chlorination--are known to be catalyzed by all radiation below a threshold wavelength of about 480 $m\mu$. Thus, wavelength effects are relatively well understood for many other chlorine processes. Without preliminary information of this kind, the selection of the most practical radiant-energy source is extremely complicated. The problem of source selection for light-catalyzed chlorine oxidation is discussed in more detail in Appendix A, p. 83.

After consideration of the problems involved in selecting the most practical radiation source, a study was undertaken to determine which wavelengths were the most effective in promoting the chlorine oxidation of wastewater.

In order to determine the effect of wavelength, it was necessary: (1) to devise a system for providing monochromatic (or nearly monochromatic) radiation at several different wavelengths, and (2) to observe the extent of organic oxidation produced by a given amount of absorbed radiation at each of those wavelengths. Not only was it necessary to establish the relative effectiveness of each ultraviolet wavelength (or group of wavelengths) between 220 and 400 $m\mu$, but it was also important to establish the contribution, if any, of visible radiation (400-700 $m\mu$). The effect of visible radiation was of particular interest because there is much unavoidable visible energy available from most commercially available sources (see Table A-I, Appendix A, p. 86).

Selection of Experimental Techniques

A number of alternatives were considered in selection of the monochromatic radiation source, design of the reaction vessel, and method of determining the amount of radiation absorbed. These alternatives are discussed in Appendix B, p. 99.

A major factor in the ultimate decision concerning experimental techniques to be employed in the wavelength-effect studies was the very recent availability of interference filters for the ultraviolet region. A series of interference filters, which permitted very effective isolation of the major wavelengths available in a high-pressure mercury arc, was obtained.

TABLE I

RESULTS OF REPRESENTATIVE EXPERIMENTS IN WAVELENGTH-EFFECT STUDY

Wavelength (mμ)	Irradiation Time (min)	Intensity (mw)	Radiant Energy (w min/gal)		Chlorine Concentration (mg/ℓ)			TOC (mg/ℓ)		
			Applied	Absorbed	Initial	Final	Difference	Initial	Final	Difference
546	120	1.20	180	1.8	95	90	5	8.2	8.8	0.0*
436	30	3.61	136	1.4	140	135	5	8.1	8.0	0.1
436	120	3.61	544	5.4	109	108	1	9.9	10.0	0.0*
405	60	2.20	167	7.7	84	80	4	8.9	9.3	0.0*
405	120	2.20	333	15.3	109	91	18	9.9	9.4	0.5
366	60	2.70	195	12.0	89	79	10	8.9	8.7	0.2
366	120	2.70	390	23.0	84	71	13	8.7	9.2	0.0*
313	60	1.04	79	13.0	99	67	32	8.4	7.4	1.0
313	130	1.04	171	29.0	118	43	75	8.4	6.5	2.1
254	20	1.15	29	12.0	92	53	39	8.9	8.9	0.0
254	40	1.15	58	23.0	90	26	64	8.5	5.9	2.6
254	60	1.15	90	32.0	68	4	64	8.8	5.1	3.7

---

* In these experiments, a small increase in TOC was observed. These anomalous results are believed to have been caused by a lack of precision in determining small differences in TOC.

The spectral energy distribution of a high-pressure mercury arc is shown in Figure 1, and the regions which could be isolated by the available interference filters are indicated.

Monochromatic Wavelength-Effect Studies

A summary of representative experiments in the wavelength-effect studies is presented in Table I. Additional experiments and details are presented in the Experimental section, p. 34.

Analysis of these results indicates that short-wavelength radiation (below 300 mμ) is the most effective in producing decreases both in TOC and in chlorine concentration. A disadvantage of long-wavelength radiation (436-546 mμ) is that it is not strongly absorbed by secondary effluents. The inability to deliver energy-per-unit-volume is a significant deterrent to the application of relatively long-wavelength radiation to this process. Because of the relatively low energy of long-wavelength radiation, and because this energy is not strongly absorbed by the effluent-chlorine solution, higher intensities of incident radiation are required in order to produce a given amount of absorbed energy. Therefore, in order to be practical, long-wave-length radiation would have to be relatively more efficient than short-wavelength radiation in producing oxidation per watt of energy absorbed. Our results, however, indicate that this is not the case.

Polychromatic Wavelength-Effect Studies

The conclusion that lower wavelengths were most effective was confirmed by polychromatic irradiation studies in which a radiation source that did not emit radiation below 300 mμ was used. The results of these experiments are presented in the Experimental section, p. 48.

In the polychromatic irradiation studies, the incident intensities were much greater than in the monochromatic irradiation studies. However, only a small fraction of this radiation was absorbed by the chlorinated effluent. The major portion of the absorbed energy was in the wavelength range 300-370 mμ.

An absorbed energy-per-unit-volume of 140 w min/gal. produced a TOC decrease of 2.4 mg/liter (see Tables XX and XXI, p. 51). However, as shown in Table I, radiation at 254 mμ will produce a TOC decrease of 2.6 mg/liter with an absorbed energy-per-unit-volume of only 23 w min/gal. Thus, the 254-mμ radiation is about six times more effective than polychromatic radiation between 300-370 mμ.

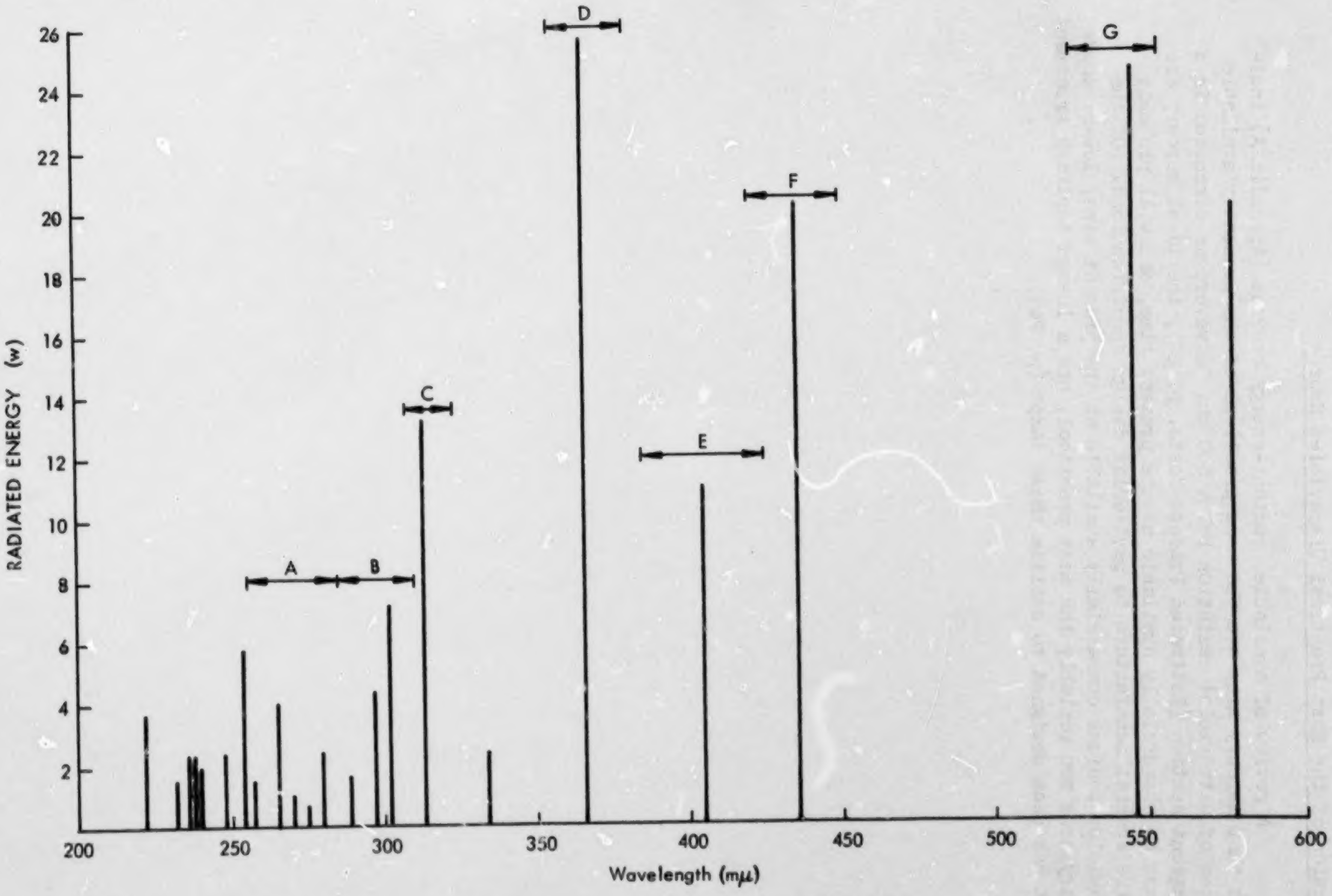

Figure 1 - Spectral Energy Distribution of High-Pressure Mercury Arc, Showing Regions (A-G) Which Could Be Isolated Using Interference Filters

Selection of the Most Practical Ultraviolet Source

A review of available, radiant-energy sources (Appendix A) indicates that mercury arcs are the most practical of the presently available sources of ultraviolet radiation below 300 mμ. However, as discussed in a subsequent section (Estimated Process Costs, p. 22), the ideal mercury arc may not be commercially available at the present time, and will probably require special manufacture to particular design specifications. Of the ultraviolet sources commercially available at the present time, low-pressure mercury arcs are probably the most practical, and a 10-mgd tertiary treatment plant has been designed to utilize these lamps (p. 24).

INTENSITY-TIME STUDIES

The relationship of radiant-energy intensity to irradiation time is a critical factor in pilot-plant design. Because of the nature of this process, the intensity of radiation will vary greatly throughout the reaction zone. The intensity will be greatest near the source, but will diminish rapidly as the distance from the source increases. The intensity at any given point is dependent upon the intensity of the source, the distance from the source and the optical properties (both absorptive and dispersive) of the reaction mixture. In order to calculate the rate of reaction at any point or throughout the reaction zone, it is necessary to establish the reaction rate which would be produced by a given amount of radiant energy. However, since the amount of radiant energy is the product of intensity multiplied by time, the relationship between these factors must be established. For example, it was necessary to determine whether 1 w of radiant energy applied for 10 min, would produce the same results as 10 w for 1 min.

Knowledge of the intensity-time relationship was also required in order to select the most effective source of radiant energy. For example, it must be determined whether one high-intensity source would be more effective than several low-intensity sources. Furthermore, since intensity decreases with distance from the source, intensity-time studies were necessary to establish the optimum depth of effluent which can be effectively treated.

The intensity-time studies were concerned primarily with radiation from low-pressure mercury arcs. These lamps are economical sources of short-wavelength radiation (254 mμ) which was known, from the wavelength-effect studies, to be highly effective in promoting the oxidation.

Intensity-Time Studies Using the Cell Reactor

Initial experiments were performed with the same equipment and procedures used in the wavelength-effect experiments. Detailed results are presented in the Experimental section, p. 50.

The results of the intensity-time studies performed, using the cell reactor, can be summarized as follows:

1. As indicated in Figure 2, there was very little effect of intensity on TOC decrease up to an absorbed energy-per-unit-volume of 30 w min/gal. At higher values of absorbed energy, lower intensities were more effective in reducing TOC.

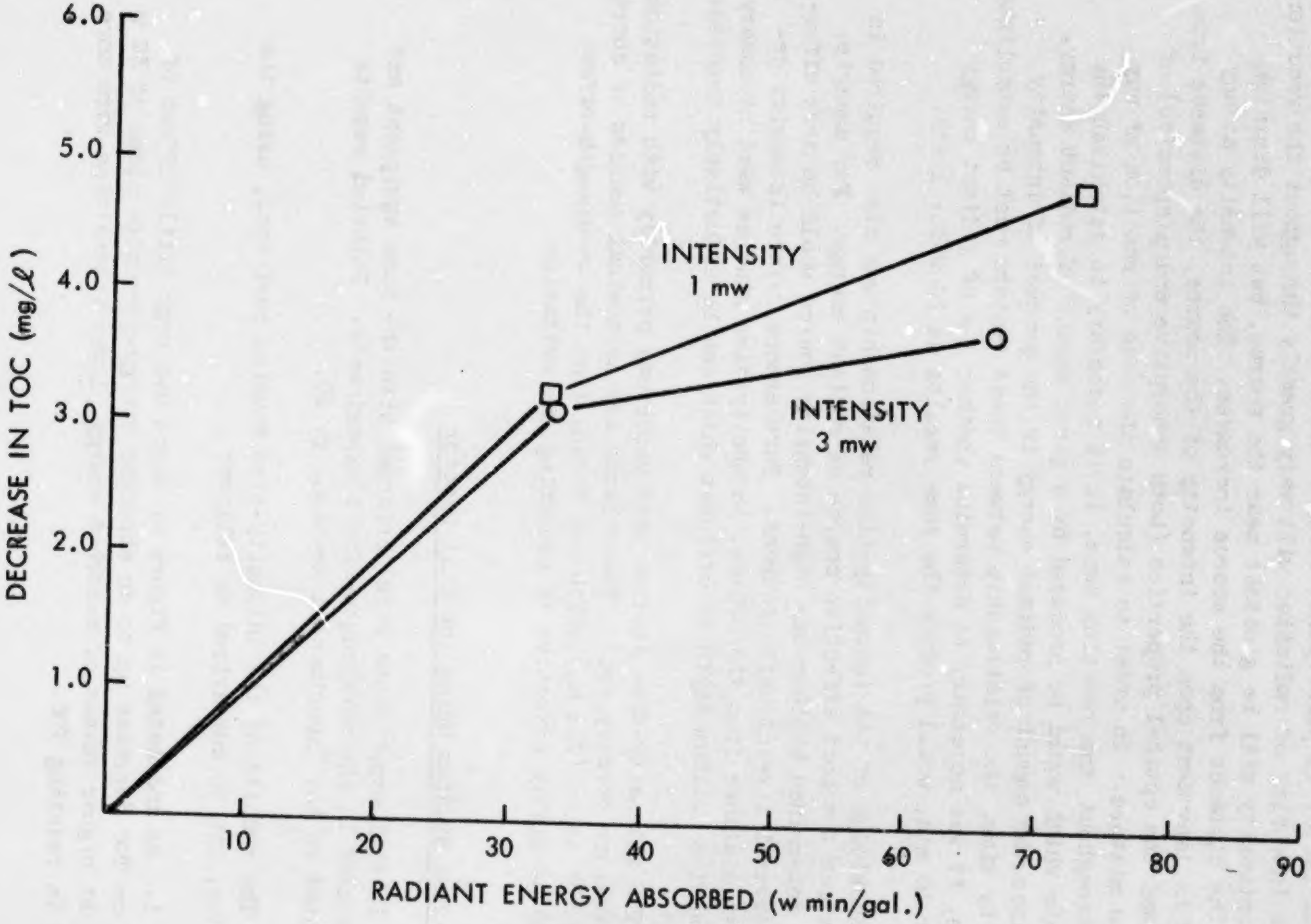

Figure 2 - The Effect of Radiation Intensity on TOC Decrease (Cell Reactor)

2. The decrease in chlorine concentration was dependent only upon total energy absorbed, regardless of intensity. Figure 3 is a plot of the decrease in chlorine concentration versus energy absorbed. The data were obtained from a series of experiments in which the irradiation time was varied from 7.5 to 101 min and the applied intensity was 1 to 3 mw. The plot in Figure 3 shows a pronounced change in slope after the absorption of radiant energy equivalent to about 50 w min/gal. At higher values of absorbed energy, the chlorine concentration was less than 10-15 mg/liter. Thus, at low chlorine concentrations the absorbed radiant energy is very much less effective in reducing chlorine concentration.

The extent of organic oxidation was measured in terms of the decrease in absorbance. The absorbance due to chlorine was subtracted from the total absorbance to obtain the absorbance due to the effluent. However, no relationship could be established between the rate of decrease in effluent absorbance and the applied intensity. Also, no relationship could be established between the effluent absorbance and the total amount of radiant energy absorbed.

Intensity-Time Studies Using the Batch-Recycle Reactor

Intensity-time data obtained, using the batch-recycle reactor, provided important information concerning the relationship of these factors (a complete discussion of the batch-recycle reactor studies is presented in the next section of this report). The most significant difference between the cell reactor and the batch-recycle reactor was that in the latter the concentration of chlorine was relatively low: 5-10 mg/liter compared to 50-100 mg/liter in the cell reactor. Also, since relatively large amounts of effluent were treated in the batch-recycle reactor, COD determinations could be obtained.

The results of two, representative, batch-recycle reactor experiments are presented in Figures 4 and 5. (Additional details are presented in the Experimental section, p. 61). The results were similar to those obtained using the cell reactor, in that low intensity was more effective than high intensity. That is, a given amount of absorbed energy would produce a greater amount of TOC and COD decrease if the energy was applied at low intensity (and, obviously, for a longer time). However, there were three important differences between the cell-reactor results and the batch-recycle reactor results:

1. The differences between low and high intensity were much more pronounced in the batch-recycle reactor experiments; low intensities were very much more effective than high intensities.

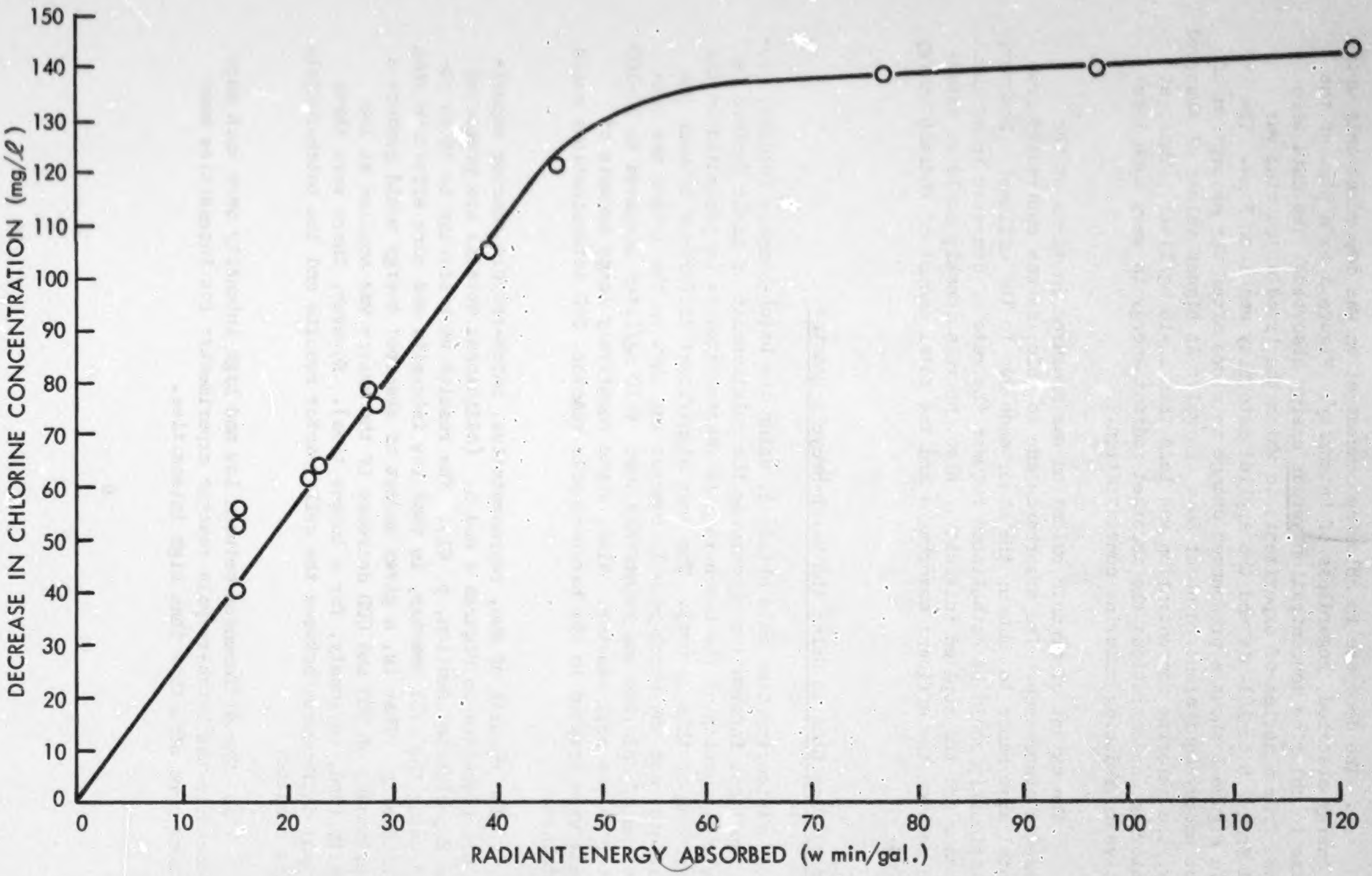

Figure 3 - The Effect of Radiant Energy Absorbed on the Extent of Chlorine Consumption

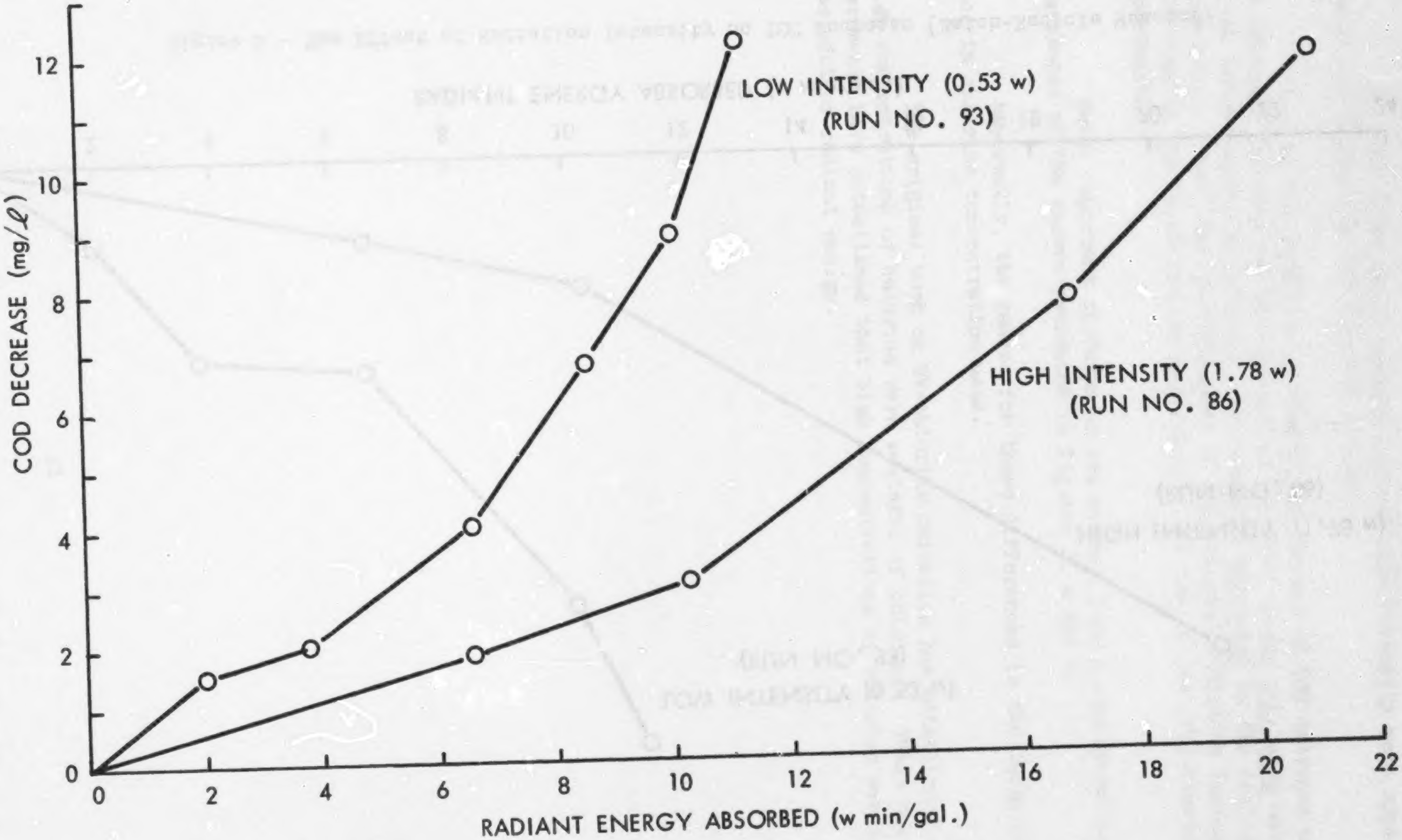

Figure 4 - The Effect of Radiation Intensity on COD Decrease (Batch-Recycle Reactor)

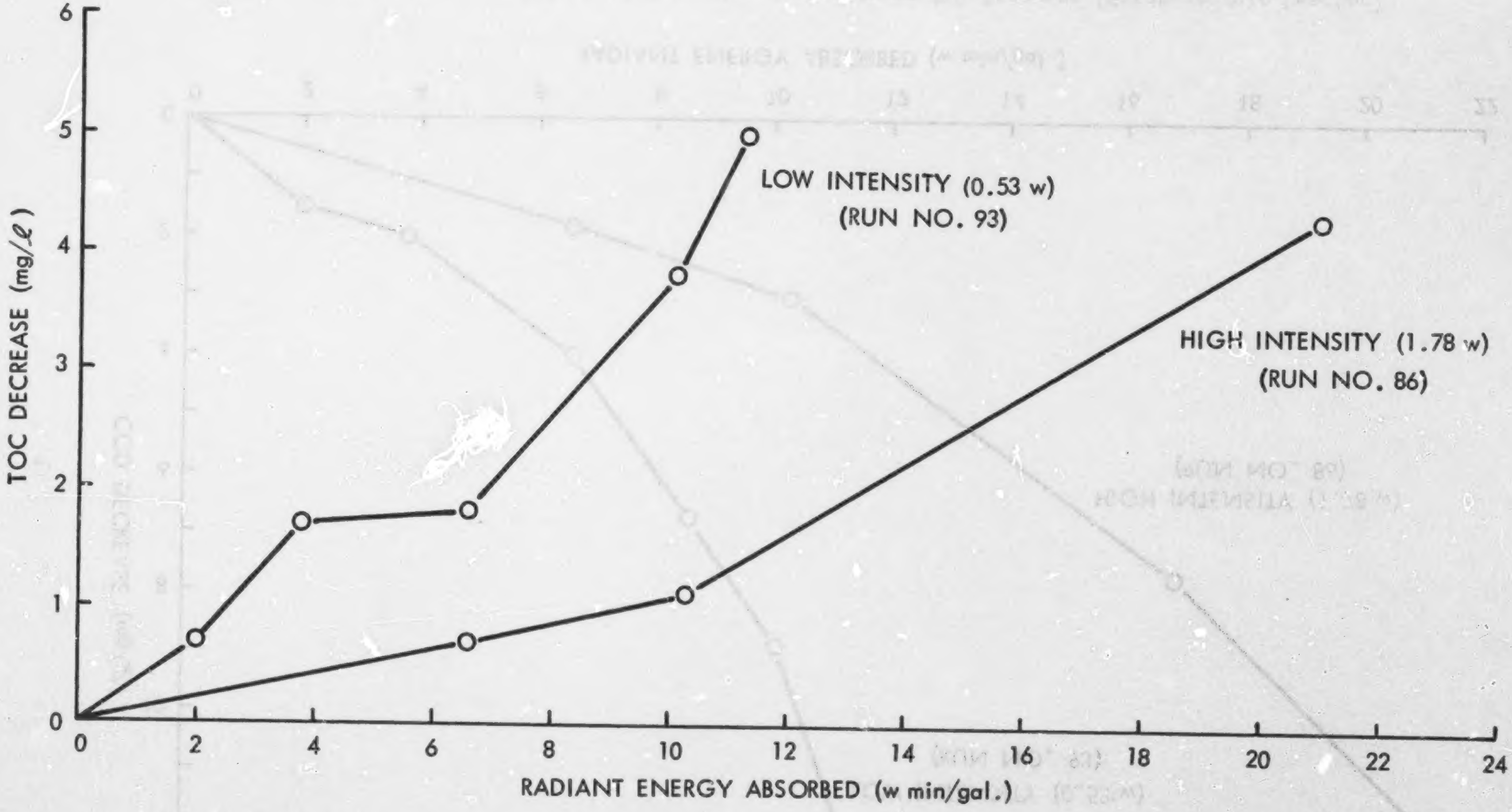

Figure 5 - The Effect of Radiation Intensity on TOC Decrease (Batch-Recycle Reactor)

2. The differences between low and high intensity were apparent even at low values for the absorbed energy.

3. As the oxidation proceeded, the amount of TOC decrease and COD decrease produced per unit amount of absorbed energy increased markedly in the batch-recycle experiments, but actually decreased in the cell-reactor experiments. Thus, the effectiveness of the absorbed radiation increased with time in the batch-recycle experiments, but not in the cell-reactor experiments.

These important differences are evident from a consideration of the shapes of the curves presented in Figures 2, 4 and 5.

Apparently, the reason for these differences is the large difference in chlorine concentration used.

The original work on UV-chlorine oxidation had established that high concentrations of chlorine were wasteful of chlorine. These new experiments have established that high concentrations of chlorine are also wasteful of radiant energy.

BATCH-RECYCLE REACTOR STUDIES

A batch-recycle reactor was constructed in order to evaluate certain design factors related to UV-chlorine oxidation. A diagram of this reactor is presented in Figure 6, and a detailed description of the reactor and operating procedures is presented in the Experimental section, p. 61. A low-pressure, mercury-arc lamp was used in this reactor because the wavelength-effect studies had indicated that this kind of lamp was the most practical of presently available, radiant-energy sources.

A reactor of this kind is especially suitable to this process for the following reasons: (1) a batch-recycle reactor is ideal for relatively slow, photochemical reactions such as this; (2) relatively large quantities of effluent can be processed; thus, analytical determinations which require relatively large samples, such as COD, are feasible; (3) an investigation of relatively low chlorine concentrations can be performed; (4) the pH can be controlled by alkali addition instead of by employing a relatively high concentration of buffer; (5) the system is dynamic rather than static, and the problems of unmixed reactors are avoided; (6) the system is similar to the ultimate system which will be applied to wastewater treatment; and (7) some critical design parameters can be established, such as optimum effluent depth, the optimum intensity of the radiant energy source, and the amount of organic oxidation which can be obtained from a given amount of absorbed energy.

A series of effluent-oxidation experiments were performed, and the results are summarized in Table II.

Additional details are presented in the Experimental section, pp. 68-79.

In each of the experiments, TOC and COD decreased at an almost constant (linear) rate. The rate of COD decrease was slightly greater than the rate of TOC decrease. These results are not greatly different from those obtained from batch reactions run during the original research on UV-chlorine oxidation (Contract No. 14-12-72).

The intensity of the radiation impinging on the chlorinated effluent was carefully measured by actinometric techniques. (See Experimental section, p. 65).

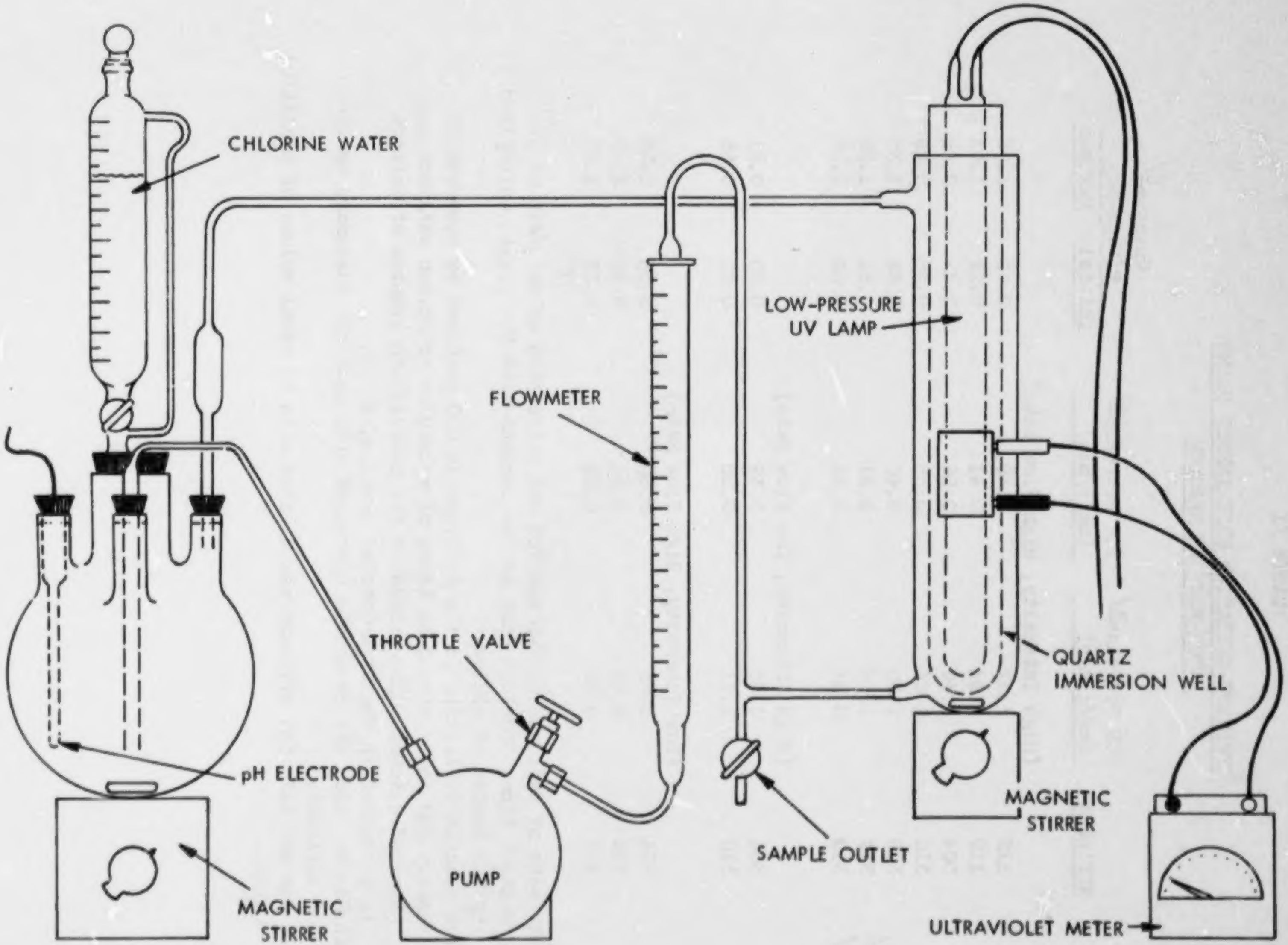
CHLORINE WATER
FLOWMETER
LOW-PRESSURE UV LAMP
THROTTLE VALVE
QUARTZ IMMERSION WELL
pH ELECTRODE
MAGNETIC STIRRER
PUMP
SAMPLE OUTLET
MAGNETIC STIRRER
ULTRAVIOLET METER

Figure 6 - Diagram of Batch-Recycle Reactor

TABLE II

EFFLUENT-OXIDATION EXPERIMENTS USING BATCH-RECYCLE REACTOR

Run No.	Effluent	COD Decrease[a] (mg/ℓ/min)	TOC Decrease[a] (mg/ℓ/min)	Quantum Efficiency[b] Initial	Quantum Efficiency[b] Maximum
		(High Intensity, High Flow Rate)			
66	112	1.31	0.38	0.42	1.36
68	112	0.94	0.41	0.21	1.04
74	304	1.46	0.56	0.47	0.55
86	310	1.04	0.35	0.25	0.89
112	319	1.30	0.40	0.62	1.33
108[c]	319	1.08	0.51	0.61	1.95
117[d]	319	0.81	0.33	0.35	1.16
		(High Intensity, Low Flow Rate)			
78	304	0.93	0.39	0.20	0.61
101	310	1.11	0.28	0.43	0.66
		(Low Intensity, High Flow Rate)			
82	304	0.83	0.60	0.58	2.36
93	310	0.69	0.31	0.70	2.48
104	319	0.70	0.25	0.33	1.47

---

[a] The rate of decrease in COD and TOC was calculated as mg/ℓ/min of UV contact time. Contact time is the contact time per cycle, multiplied by the number of cycles.

[b] The quantum efficiency is the decrease in COD produced by absorbed UV energy and is expressed in terms of molecules of oxygen utilized per absorbed quantum. The procedure for calculating quantum efficiency is presented in the Experimental section, p. 96.

[c] In Run No. 108, the reservoir contained only half the customary amount of effluent.

[d] In Run No. 117, the effluent was diluted with an equal volume of distilled water.

The fraction of radiation absorbed was also accurately determined at various times during the reaction (this procedure is also described in the Experimental section, p. 64). The fraction of radiation absorbed also decreased as the oxidation proceeded, but not at a constant rate; the rate of decrease was greater during the first part of the oxidation than it was during the last part.

The rate and extent of decrease in the fraction of radiation absorbed were of particular interest because this phenomenon has important implications in regard to reactor design and quantum efficiency. The EDP (effective depth of penetration; the depth at which 90% of the radiation is absorbed) can be calculated from the absorbance data (cell length in centimeters, divided by absorbance). At the beginning of a typical experiment, the EDP is about 9 cm and increases to 40-50 cm at the end of the experiment. A commercially feasible reactor must obtain maximum use of emitted radiation. In order to accomplish this, some provision for the change in EDP must be made. Either the effluent depth must be greater toward the end of the treatment, or some method of utilizing the most efficient average radius must be derived. (Thorough mixing of the reactor, or recycling of treated effluent, might permit effective use of a constant-depth reactor.)

As a result of both the constant rate of COD decrease and the decrease in radiation absorbed, the effectiveness of the absorbed radiation increased as the oxidation proceeded.

Experiments with the batch-recycle reactor permitted very accurate determination of the effectiveness of the absorbed radiation in producing a given amount of organic oxidation. By definition, the term "quantum efficiency," (E), is a measure of the effectiveness of the absorbed radiation in which the extent of organic oxidation is expressed as the number of molecules of oxygen which have been utilized, and the absorbed energy is expressed in quanta. Thus, "quantum efficiency" is analogous to the term "quantum yield" which is generally used in photochemistry. The procedure followed in calculating quantum efficiency is presented in the Experimental section, p. 80.

In each experiment, the quantum efficiency increased as the oxidation proceeded, although there were very wide differences in the maximum quantum efficiencies which could be attained.

Investigation of High Intensity and High Flowrate

The results obtained with maximum lamp intensity (1.78 w) and high flowrate (665 ml/min) are presented in the first part of Table II. There was considerable variation in the rates of COD and TOC decrease; the rate of COD decrease ranged from 0.94 to 1.31 mg/liter/min, and the rate of TOC decrease ranged from 0.35 to 0.55 mg/liter/min.

These variations apparently cannot be correlated with the initial absorbance of the effluent; in some experiments a higher initial absorbance was accompanied by a faster rate of COD decrease, and in other experiments the reverse was true. In Run No. 117, the effluent (MRI 319) was diluted with an equal volume of distilled water. The decrease in absorbance caused by the dilution did not produce a proportional decrease in oxidation rate.

In Run No. 108, only one-half of the customary amount of effluent was placed in the reservoir. This procedure effectively doubled the total contact time in the reactor for the same flowrate and elapsed time. Also with half as much effluent in the reservoir, the amount of "dark time" was decreased by about one-half; that is, for a specified amount of irradiation time, the reaction mixture spends only half as much time in the dark when the reservoir is only half filled. If a significant "dark reaction" occurred, then higher oxidation rates would be expected if the reservoir were completely filled. A comparison of Run No. 112 with Run No. 108 (Table II) shows that the rate of COD decrease was greater with an increased amount of dark time. This indicates that some decrease in COD was occurring in the dark. However, the rates of TOC decrease show the opposite effect; i.e., the rate of TOC decrease was considerably greater when the dark time was minimized. In both experiments, the quantum efficiency increased at a rate proportional to the extent of COD decrease.

Investigation of High Intensity and Low Flowrate

The results of experiments performed at flowrates less than half those employed in the high-flowrate experiments are shown in the second part of Table II. In the low-flowrate experiments the total contact time (irradiation time) is the same as in the high-flowrate experiments. The reason is that at the low flowrate a given portion of the reaction mixture passes more slowly through the reactor, but it passes through a fewer number of times. Within experimental error, flowrate (as expected) does not appear to affect the rates of TOC or COD removal, nor does flowrate affect the quantum efficiency.

Investigation of Low Intensity and High Flowrate

The results of experiments performed at low intensities (0.53 w compared with 1.73 w) are presented in the last part of Table II. A comparison of rates of COD and TOC decrease shows that the large decrease in intensity did not greatly affect the organic oxidation rate. (In fact, the rate of TOC decrease in Run No. 82 was the fastest observed.)

Obviously, the low-intensity radiation was more efficient, and this fact was indicated by the quantum efficiency calculations. At all levels of absorbed radiation, the low-intensity radiation had about twice the quantum efficiency as the high-intensity radiation.

Preliminary Investigation of Minimum Chlorine Requirement

Toward the end of the experimental period, a preliminary investigation was made of the possibility of using less-than-stoichiometric amounts of chlorine. In these experiments, chlorine was added to bring the initial chlorine concentration to about 5 mg/liter, but the chlorine concentration was allowed to decrease to zero before additional chlorine was added. The results of these experiments are described in the Experimental section, p. 67. Less-than-stoichiometric amounts of chlorine were required under these conditions, but some loss in overall, organic, reaction rate was apparent. Possibly an optimum chlorine concentration below 5 mg/liter could be established at which maximum oxidation rates could be maintained with minimum amounts of chlorine consumed.

The effect of oxygen under these conditions has not yet been established. However, the preliminary experiments have indicated that a surplus of oxygen does not increase the reaction rate, nor does it affect the amount of chlorine consumed. The role of oxygen in the UV-chlorine process is discussed in the next section of this report.

OXYGEN-EFFECT STUDIES

The results of numerous photochlorination experiments published in the literature suggest that dissolved oxygen might have a profound influence on the catalyzed chlorine oxidation. For example, traces of oxygen produce a strong inhibiting influence on organic photochlorinations. Furthermore, there are some well-known photocatalyzed reactions of chlorine with oxygen.

Since the photochemical chlorine oxidation takes place in an effluent that has been subjected to extended aeration and is thus nearly saturated with air, it is possible that oxygen (or products of the reaction of oxygen with chlorine) are vitally involved in the organic oxidation. Oxygen, or oxygen-chlorine reaction products, could act as inhibitors or promoters of the organic oxidation. Perhaps dissolved oxygen could act as a major oxidizing agent, and effective organic oxidation could be achieved using oxygen in the presence of only small smounts of chlorine. Conversely, if oxygen is an inhibitor of the chlorine oxidation, then perhaps more rapid oxidation and more efficient use of chlorine could be achieved if all oxygen were excluded from the system.

A series of experiments was performed in order to check these possibilities. The equipment used was the 5-liter reactor used in the original UV-chlorine work.

In the first experiment, the effluent was saturated with oxygen, and oxygen was continuously supplied to the effluent-chlorine mixture during the additions. In the second experiment, the dissolved oxygen was purged with nitrogen, and a positive nitrogen pressure was maintained during the oxidation. In the third experiment, no treatment of the reaction mixture with either oxygen or nitrogen was employed.

In all three experiments, the rates and extents of COD and TOC decreases were about the same (details are presented in the Experimental section, p. 58). Apparently, oxygen had no effect on the rate of oxidation. Certainly, the results show that oxygen had no inhibitory effect.

In subsequent work employing a batch-recycle reactor, a question arose: is it possible to use less-than-stoichiometric amounts of chlorine in this process? Preliminary experiments indicated that the answer was affirmative. If so, then molecular oxygen is very probably the oxidizing agent which accounts for the organic oxidation achieved in excess of that accomplished by chlorine.

The experiments described in this section do not contradict this possibility. Under the conditions investigated, a large concentration of chlorine and a relatively small concentration of oxygen were involved. Under these conditions, it would not be possible to detect whether or not significant amounts of oxygen were actually consumed during the experiments.

To verify this possibility, additional experiments are required in which (1) minimum concentrations of chlorine are employed and (2) careful measurement is made of the amount of chlorine consumed and of the organic oxidation accomplished.

ESTIMATED PROCESS COSTS

Process costs have been estimated for the large-scale application of the UV-chlorine process to wastewater. Two major factors affect these estimates: (1) the kind of ultraviolet source used, and (2) the amount of oxidation which can be accomplished by a given amount of applied radiation. As discussed below, the wavelength-effect studies have shown that low-pressure, mercury-arc lamps are most probably the best, presently available, radiation sources. Also, preliminary data from the batch-recycle reactor studies have provided a useful estimate of the effectiveness of the applied radiation.

Radiant Energy Source

A primary object of this research effort was to obtain information which would permit the selection of the most practical, radiant-energy source. The wavelength-effect studies have indicated that wavelengths shorter than 300 mμ are the most effective. A consideration of available sources (see Appendix A) indicated that the most practical sources of this kind of radiation at the present time are mercury-arc lamps.

There are two general types of mercury-arc lamps: low-pressure and high-pressure arcs. High-pressure arcs emit a broad spectrum of UV wavelengths between 220 and 366 mμ. Low-pressure lamps emit radiation almost exclusively in the region of 254 mμ. High-pressure arcs emit much-more-intense radiation than low-pressure arcs of about the same size. Also, the high-pressure arcs are usually short, typically less than 1 ft in length. Low-pressure arcs can be of almost any length, and lamps 5 ft in length are commercially available. The useful life of high-pressure arcs is relatively short--usually less than 1,000 hr; low-pressure lamps have long lifetimes--usually 7,500 hr or longer. High-pressure arcs are more expensive than low-pressure arcs, but do not have the relatively high electrical efficiency of the low-pressure arcs.

It should be emphasized that there are many variables in the construction of mercury-arc lamps and that certain design changes are possible which can maximize the usefulness of a mercury arc for specific purposes. For example, higher intensities can be produced from low-pressure arcs by the application of higher voltages. The higher intensity is not obtained without some concessions; for example, shorter lifetimes or lower electrical efficiency is usually the result of the application of higher voltages.

Low-pressure mercury arcs are commonly used for the sterilization of water and are designed to emit the germicidal wavelengths with high efficiency. Prominent manufacturers of this kind of equipment were contacted when it became evident that low-pressure arcs might also be useful for the UV-chlorine oxidation process. It was somewhat surprising to learn that most of the manufacturers were dissatisfied with commercially available arcs; for example, one company imports specially made arcs from Europe, and another company manufactures its own arcs.

Because of the present state of the art of UV lamp manufacture, it is highly probable that the ideal mercury arc for the UV-chlorine process is not presently commercially available, but will require special manufacture to particular design specifications.

However, for the current review of process costs, commercially available low-pressure mercury arcs have been selected because they represent the nearest approximation to the kind of UV source that will be needed.

The main disadvantage of presently available, low-pressure arcs is their relatively low intensity which, in turn, necessitates the use of a very large number of lamps. Similar lamps of much higher intensity can probably be produced. Lamps of two or three times the intensity of presently available lamps would permit significant reduction in plant investment costs--perhaps as much as 3.00¢/1,000 gal. However, the increased intensity could probably not be obtained without an offsetting loss of lamp lifetime or of electrical efficiency. Therefore, the estimated lamp costs and power costs probably represent a close approximation of the actual operating costs.

The experimental results show that low-intensity radiation produces higher quantum efficiencies. The advantage of low-intensity radiation would not be seriously offset by a substantial increase in the intensity of the source. This apparent contradiction is explained by the fact that regardless of the intensity of the source, most of the effluent in a reactor which is designed for optimum utilization of the radiant energy is actually treated with low-intensity radiation because of attenuation factors. For example, for a typical effluent in a cylindrical, concentric reactor, over half of the incident radiation would be absorbed by only 10% of the liquid located nearest to the radiant-energy source. The next 10% fraction of effluent would be exposed to radiation of less than one-half the incident intensity. Thus, the bulk of the effluent affected by the radiation would be absorbing radiation at relatively, very low intensity.

Effectiveness of the Applied Radiation

The batch-recycle reactor studies provided the first realistic estimate of the effectiveness of radiation from a low-pressure mercury arc. These experiments are described in detail in the section of this report entitled "Batch-Recycle Reactor Studies," p. 61. The effectiveness of the applied radiation was determined as the "quantum efficiency," defined as the number of molecules of oxygen utilized per quantum absorbed. Two surprising observations were made: first, the quantum efficiency increased as the oxidation proceeded, and second, the quantum efficiency was greater if the applied intensity were decreased.

In the present process-cost estimation, it was assumed that the quantum efficiency is equal to the average quantum efficiency (1.30) obtained in two of the low-intensity experiments (Table II). This assumption is a conservative one because most of the reaction mixture in a practical reactor will be exposed to very low intensities. In the proposed large-scale reactor design, low intensities can be employed efficiently because of allowance for long contact time; the contact time in the proposed reactor is about 40 min, or almost four times longer than the contact times examined in the batch-recycle reactor studies.

Plant Description

A process flowsheet for a plant handling 10-million gal./stream day is presented in Figure 7. The plant has been designed to reduce the COD from 25 to 10 mg/liter using the G64T6, low-pressure, mercury-arc lamp. This lamp is in commercial production. The UV output is 18.5 w for an electrical input of 65 w. A plant treating 10-million gal./day would require 4,020 lamps.

To reduce the COD from 25 to 10 mg/liter, the stoichiometric amount of chlorine required is 67 mg/liter. This chlorine would be added continuously to the wastewater at four points in the "reactor flume." Since the effectiveness of the UV-catalyzed chlorine oxidation is influenced by pH, provision was made for the addition of caustic at two points in the "reactor flume."

The plant would provide 10 reactor flumes with a depth of 4.5 ft, a width of 5.5 ft and a length of 160 ft. Each flume would contain 402 lamps enclosed in quartz tubes. Four horizontal lamps are placed in vertical rows 12 in. apart in the front section of the flumes. Only three lamps in vertical rows 20 in. apart would be needed in the last part of the flumes. This spacing of lamps permits absorption by the effluent of practically all the radiation and also allows for the decrease in absorption as the reaction proceeds.

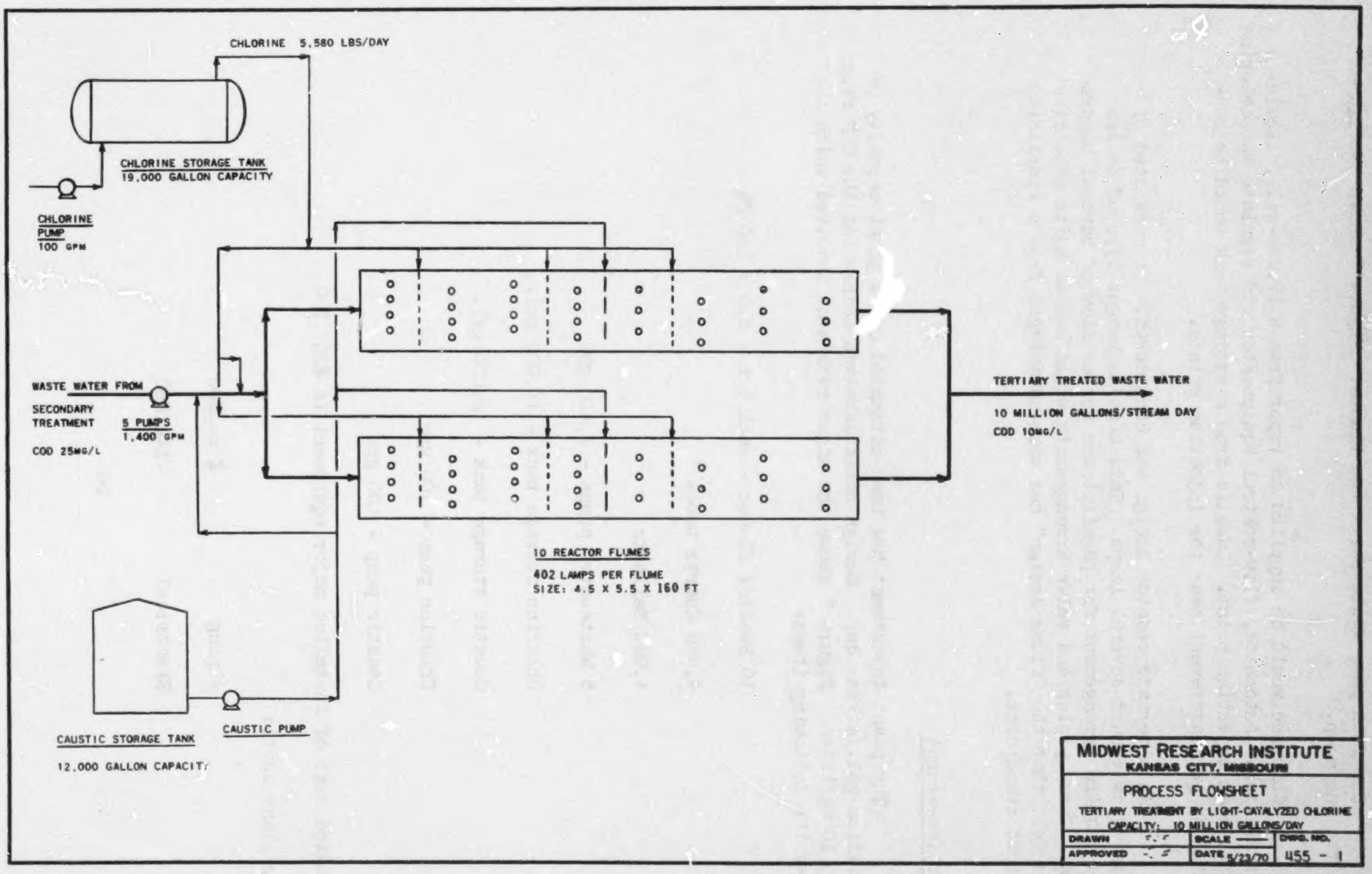
CHLORINE 5,580 LBS/DAY
CHLORINE STORAGE TANK
19,000 GALLON CAPACITY
CHLORINE PUMP
100 GPM
WASTE WATER FROM
SECONDARY TREATMENT
COD 25MG/L
5 PUMPS
1,400 GPM
10 REACTOR FLUMES
402 LAMPS PER FLUME
SIZE: 4.5 X 5.5 X 160 FT
TERTIARY TREATED WASTE WATER
10 MILLION GALLONS/STREAM DAY
COD 10MG/L
CAUSTIC STORAGE TANK
12,000 GALLON CAPACITY
CAUSTIC PUMP
MIDWEST RESEARCH INSTITUTE
KANSAS CITY, MISSOURI
PROCESS FLOWSHEET
TERTIARY TREATMENT BY LIGHT-CATALYZED CHLORINE
CAPACITY: 10 MILLION GALLONS/DAY
DRAWN
APPROVED
SCALE ——
DATE 5/23/70
DWG. NO.
455 - 1

Figure 7 - Process Flowsheet for Tertiary Treatment by Light-Catalyzed Chlorine, Capacity 10-Million Gal./Day

One feed pump would serve two flumes. Figure 7 shows two flumes with the one pump.

Chlorine would be supplied as vapor from a 19,000-gal., liquid-chlorine tank. Automatic, flow-control equipment would regulate the chlorine flow to each injection point. Caustic from a storage tank would be controlled by pH measurement near the injection points.

An alternate reactor design was considered. It consisted of annular flow around several lamps. This heat-exchanger type of design would require arrangement for parallel and series flow of several hundred units. Thus, piping and valve arrangements would become quite extensive. It is felt that the "flume design" has more advantages from a simplicity and cost standpoint.

Plant Investment

The plant investment has been estimated for a plant capacity of 10-million gal./stream day. Design basis involves decreasing the COD from 25 to 10 mg/liter. Figure 7 shows the major equipment involved which includes the following items:

10 Reactor flumes - each 4.5 x 5.5 x 160 ft

4,020 Quartz tubes

4,020 Ballasts

5 Wastewater pumps - 1,400 gpm

Chlorine storage tank - 19,000 gal.

Caustic storage tank - 12,000 gal.

Chlorine pump - 100 gpm

Caustic pump - 100 gpm

Estimated cost of installed major equipment is $257,500.

Other plant costs:

Piping	$ 54,300
Electrical	144,000

Instrumentation	$102,000
Painting	17,000
Subtotal	$574,800
Contingency	57,480
Contractor and engineering	86,220
	$718,500

A building 130 x 190 ft would be required to house all 10 reactor flumes, control equipment, office and lab. Using two acres for the plant site, the building and site costs have been estimated as

Site	$ 24,000
Building 130 x 250 ft	247,000
	$271,000

This gives a total plant investment of $989,500, excluding lamp costs. The G64T6 lamp has a life expectancy of one year. Therefore, it is felt this cost item of $56,200 is better treated as a yearly operating cost under the next section.

Treatment Cost

Treatment cost was estimated as follows:

	Annual	¢/1,000 gal.
Labor: 2 men/shift at $350	$ 61,320	1.86
Labor overhead: 50%	30,680	0.93
Raw materials		
Chlorine: 5,580 lb/day at 3.75¢	69,000	2.09
Caustic: 2,000 lb/day at 3.30¢	21,780	0.66

Utilities		
Fuel gas: 25¢/MM Btu	600	0.02
Electricity: 456 kw at 1.0¢/kw-hr	36,100	1.09
Lamps: 5,680 at $14	56,200	1.70
	$275,680	8.35¢

Fixed charges on the investment of $989,500 have been estimated as

	Annual	¢/1,000 gal.
Depreciation over 20 years	$ 49,475	1.50
Interest at 4%	23,800	0.72
Insurance at 1%	9,895	0.30
Maintenance at 3%	29,685	0.90
	$112,855	3.42¢

The total treatment costs are $388,535 annually, including fixed charges on investment and operating costs. The unit-cost total is 11.77¢/1,000 gal. of wastewater treated.

By placing the 10 reactor flumes outside the building, costs could be reduced an estimated $137,000. The plant investment would drop to $852,500, and the fixed charges would be reduced by $15,600 annually. Total unit costs would then be 11.30¢/1,000 gal.

Substantial reductions in cost would be possible if (1) more intense, longer-lived, or more efficient mercury-arc lamps were available, (2) higher quantum efficiencies could be obtained, or (3) less-than-stoichiometric amounts of chlorine were required.

The estimate of the cost of caustic was based on the experimentally observed amount required to maintain the optimum pH of 5.0. Considerabley less caustic would be required if the pH did not require adjustment. Experimental determination of the economic consequences of operating at ambient pH has not been made.

Consideration was also given to the cost of treating effluents of higher COD content. Because of the longer reaction time required for effluents of this kind, a higher quantum efficiency (3.72) could be reasonably presumed. An adjusted estimate of the cost of reducing the COD of an effluent from 45 mg/liter to 10 mg/liter is presented below:

	Cost (¢/1,000 gal.)	
Labor	1.86	
Labor overhead	0.93	
Chlorine	4.88	
Caustic	1.54	
Fuel gas	0.02	
Electricity	0.96	
Lamps	1.22	11.40
Investment: \$989,500		
$\left(\frac{35}{15}\right)^{0.7}\left(\frac{1.30}{3.72}\right)^{0.7}$	= 860,000	2.97
		14.38

The above estimate clearly shows the relatively high contribution to cost made by chlorine and caustic, and it suggested further study. These factors were investigated toward the end of the research program using the batch-recycle reactor. Preliminary data (see Experimental section, p. 67) indicated that up to one-third less than the stoichiometric amount of chlorine could be employed. This savings in chlorine would amount to 1.6¢/1,000 gal. in the above cost estimate.

EXPERIMENTAL

Actinometer Procedures and Calculations

All of the actinometer experiments were performed in a darkroom equipped with a red safelight. Ultraviolet and visible absorbances were obtained using a Beckman DU spectrophotometer which was located in the darkroom. Most of the procedures and calculations are similar to those recommended by Calvert and Pitts.1/

Calibration of Monochromatic Wavelength Sources

Solutions of 0.00600 M ferric chloride and 0.01800 M potassium oxalate were prepared. A 10-ml portion of each was placed in a brown bottle protected from light with aluminum foil. The ferrioxalate solution was pipetted into a cylindrical quartz cell of 1.0-cm lightpath and 2.2-cm diameter (volume 2.65 ml). The cell was placed in the irradiation chamber, as near to the interference filter as possible, and was irradiated. The high-pressure, mercury-arc lamp had been allowed to warm up prior to placing the cell in the holder.

The number of ferrous ions ($N_{Fe^{++}}$) produced can be calculated from the following equation:

$$N_{Fe^{++}} = \frac{6.023 \times 10^{20}\ V_1 V_3 \log (I_o/I)}{V_2 \ell \varepsilon}$$

where V_1 = volume of actinometer solution irradiated (2.65 ml).

V_2 = volume of aliquot taken for analysis (2.00 ml).

V_3 = final volume to which aliquot, V_2, is diluted (5.00 ml).

$\log (I_o/I)$ = absorbance of solution at 510 mμ.

ℓ = path length of spectrophotometer cell used (1.00 cm).

ε = experimental value of the molar extinction coefficient of the ferrous complex (1.11×10^4 liters/mole-cm).

Thus, for this system, $N_{Fe^{++}} = 3.67 \times 10^{17} \times A$, where A is the difference between the absorbance of the irradiated and nonirradiated actinometer solutions.

The intensity of the light beam, incident just within the photocell reactor front window (I_o^i), can be calculated from the following equation:

$$I_o^i = \frac{N_{Fe^{++}}}{\varphi\ t\ \left(1-10^{-\varepsilon[A]\ell}\right)}\ \text{quanta/sec,} \qquad (1)$$

where φ = the quantum yield of the actinometer reaction at the particular wavelength.

t = the irradiation time (sec).

ε = the molar extinction coefficient of the actinometer solution at that wavelength.

$[A]$ = the concentration of the actinometer solution.

ℓ = length of the cell.

The quantity, $(1-10^{-\varepsilon[A]\ell})$, is the fraction of the incident light absorbed by the actinometer and can be measured experimentally using a spectrophotometer (1-T, where T = transmittance), or it can be calculated from known values of ε, A and ℓ.

The selected procedure for determining the amount of ferrous iron formed by the oxidation of oxalate by ferric iron was similar to that of Hatchard and Parker[2] and is described by Calvert and Pitts.[1] An exception is that smaller volumes have been employed. A solution of ferrous sulfate (5.06×10^{-4} M) in 0.1 N H_2SO_4 was freshly prepared from 0.1012 M ferrous sulfate standardized (by titrating an aliquot of standard dichromate) just prior to use. Portions of the dilute ferrous sulfate solution (0, 0.1, 0.2, 0.4, 0.6, and 0.9 ml) were mixed with 2 ml of 0.1 N H_2SO_4, 8 drops of 0.1% 1,10-phenanthroline in water, 1 ml of buffer (600 ml of 1 N sodium acetate and 360 ml of 1 N H_2SO_4 diluted to 1 liter), and the resulting solution was diluted to 5.0 ml in a volumetric flask and allowed to stand in the dark for 1 hr. The absorbance of these solutions was determined, and a linear plot of absorbance versus concentration was obtained having a slope in excellent agreement with the 1.11×10^4 liters/mole-cm reported by Calvert and Pitts.

Calibration of Polychromatic Wavelength Sources: The following is a derivation of the equation used to calculate the total intensity of a polychromatic source using the ferrioxalate actinometer.

The intensity of radiation just within the cell-reactor front window is determined from Eq. (1).

Conversion from quanta/sec to watts results in the following:

$$I_{tot} = \frac{k\ N_{Fe^{++}}}{\varphi\ t\ (1-T)\lambda}\ \text{watts} \qquad (2)$$

λ = wavelength in mμ.

k = constant (19.86×10^{-17} mμ·w·sec/quantum).

T = transmittance.

Transposition of the equation gives the following:

$$\frac{k\ N_{Fe^{++}}}{t} = I_{tot}\ \varphi\ (1-T)\lambda \qquad (3)$$

The number of ions formed at each separate wavelength can be calculated using the following equation:

$$\frac{k\ N_{Fe^{++}}}{t} = I_{\lambda}\varphi_{\lambda}\ \lambda\ (1-T)_{\lambda}\ , \qquad (4)$$

where λ = the discrete wavelength considered.

The total number of ions is the same sum of the ions formed at each separate wavelength.

$$\frac{k\ N_{Fe^{++}tot}}{t} = \sum_{\lambda} \frac{k\ N_{Fe^{++}}}{t} = \sum_{\lambda} I_{\lambda}\varphi_{\lambda}\ \lambda\ (1-T)_{\lambda} \qquad (5)$$

The intensity at each wavelength can be calculated from the following equation, provided that information is available concerning the output as a function of wavelength:

$$I_{\lambda} = I_{tot}\ (F_{\lambda}/F_{tot})$$

Substitution into Eq. (5) gives:

$$\frac{k\ N_{Fe^{++}tot}}{t} = \sum_{\lambda} I_{tot}\ (F_\lambda/F_{tot})\ \lambda\ \varphi_\lambda\ (1-T)_\lambda \qquad (7)$$

Removing the constant term (I_{tot}) gives:

$$\frac{k\ N_{Fe^{++}tot}}{t} = I_{tot} \sum_{\lambda} (F_\lambda/F_{tot})\ \varphi_\lambda\ (1-T)_\lambda \qquad (8)$$

Solving for the total intensity yields the following equation:

$$I_{tot} = \frac{k\ N_{Fe^{++}}}{t \sum_{\lambda} \lambda\ (F_\lambda/F_{tot})\ \varphi_\lambda\ (1-T)_\lambda} \qquad (9)$$

The equation for $N_{Fe^{++}}$ taken from Calvert and Pitts[1/] is:

$$N_{Fe^{++}} = \frac{6.023 \times 10^{20}\ V_1 V_3 \log (I_o/I)}{V_2 \ell \epsilon} \qquad (10)$$

V_1 = 3.00 ml = volume of actinometer solution irradiated.

V_2 = 2.00 ml = volume of aliquot taken for analysis.

V_3 = 5.00 ml = final volume to which the aliquot, V_2, is diluted.

$\log \frac{I_o}{I} = A_{510}$ = absorbance of actinometer solution at 510 mμ.

ℓ = 1 cm = path length of spectrophotometer cell used.

$\epsilon = 1.11 \times 10^4$ liter/mole-cm = experimental value of the molar extinction coefficient of the Fe^{++} complex as determined from the slope of the calibration curve.

Substituting the known values for k, V_1, V_2, V_3, ℓ and ϵ into Eq. (9) yields the expression used to calculate the intensity of polychromatic radiation:

$$I_{tot} = \frac{A_{510} \times 80.82}{t \sum_{\lambda} \lambda \, (F_\lambda / F_{tot}) \, \varphi_\lambda \, (1-T)_\lambda} \qquad (11)$$

Monochromatic Wavelength-Effect Experiments

Equipment: All equipment for the wavelength-effect studies was located in a separate laboratory which was converted to a darkroom and was equipped with a red safelight.

A diagram of the apparatus constructed for use in the monochromatic irradiation studies is presented in Figure 8. A 22-mm-diameter circular hole was cut in one end of a 4-in. x 6-in. metal box. A holder for the 2-in. x 2-in. interference filters was attached to the outside of the box. A cell holder was placed inside the box in such a manner that a quartz cell could be located very near to the interference filter or could be located up to 5 in. away from the filter. The inside of the box was covered with a black nonreflecting cloth which provided a light-tight seal when the box was closed.

The ultraviolet source used in most of the experiments was a "Universal Point Source", Model 401, supplied by PEK Labs, Inc., of Sunnyvale, California. This source is equipped with a power supply which permits adjustment of the current. The high-pressure mercury arc was enclosed in a housing equipped with a photographic-type variable aperture to permit adjustment in radiant-energy output. A new opening in the back of the lamp housing was made in order to locate the source closer to the interference filter. To obtain precise timing of the actinometer exposures, a simple shutter was devised to cut off all radiation from the cell before and after irradiation.

The optical characteristics of the interference filters are presented in Table III.

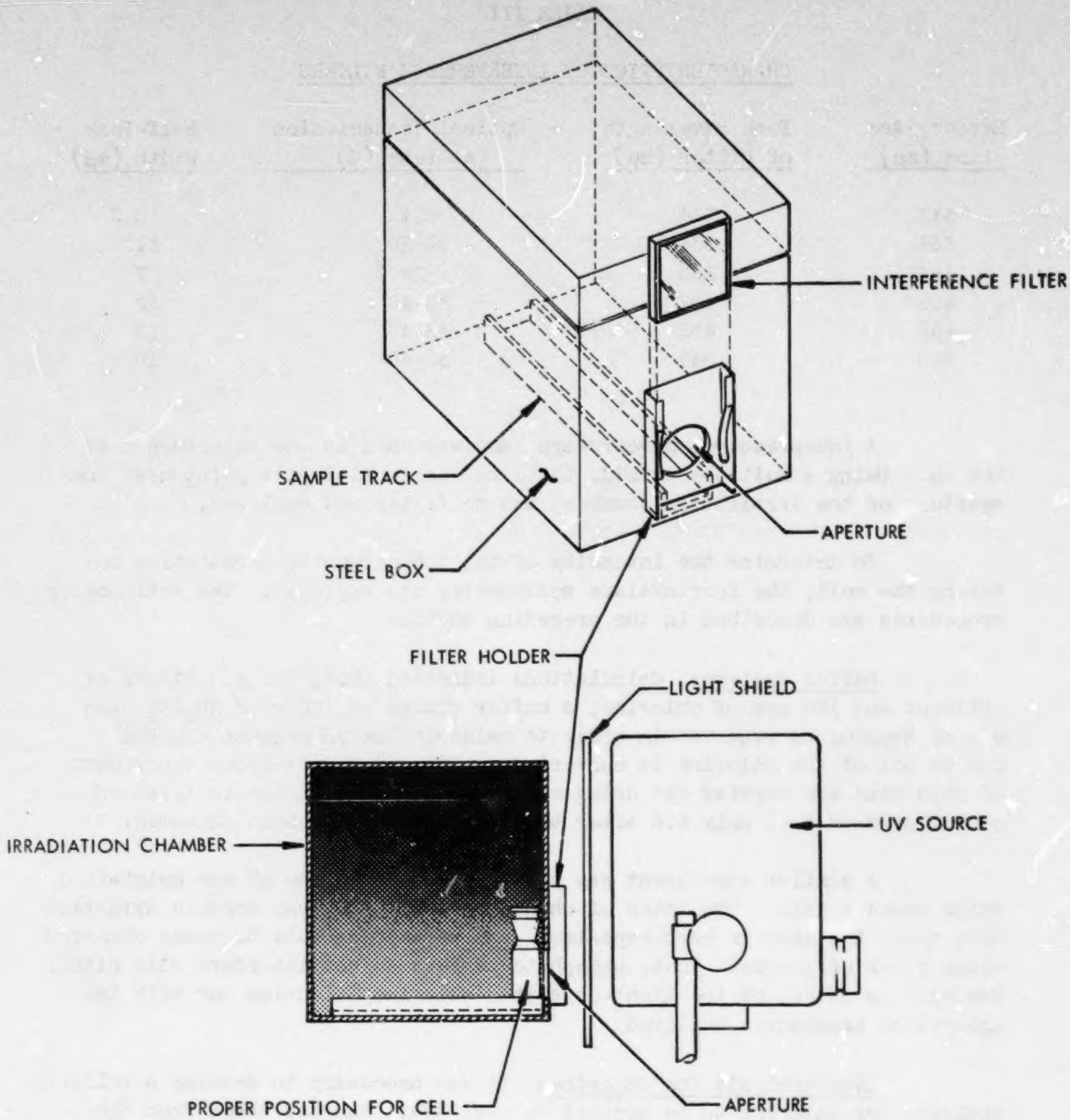
INTERFERENCE FILTER
SAMPLE TRACK
APERTURE
STEEL BOX
FILTER HOLDER
LIGHT SHIELD
UV SOURCE
IRRADIATION CHAMBER
PROPER POSITION FOR CELL
APERTURE

Figure 8 - Apparatus Used in Wavelength-Effect Studies

TABLE III

CHARACTERISTICS OF INTERFERENCE FILTERS

Mercury-Arc Line (mμ)	Peak Wavelength of Filter (mμ)	Optical Transmission at Peak (%)	Half-Peak Width (mμ)
313	314	24	6.5
334	334	10-20	11
366	363	29.5	7
405	407	35-40	12
436	435	35-40	10
546	541	35-40	10

A low-pressure, mercury-arc lamp was used in the experiments at 254 mμ. Using a suitable shield, the lamp was located at a point near the aperture of the irradiation chamber, and no filter was employed.

To determine the intensity of the monochromatic irradiation entering the cell, the ferrioxalate actinometer was employed. The actinometer procedures are described in the preceding section.

Buffer Systems: Calculations indicated that, for 4.0 liters of effluent and 190 ppm of chlorine, a buffer charge of 102 g of KH_2PO_4 and 2 g of Na_2HPO_4 is required in order to maintain the pH between 4.5 and 5.5 as all of the chlorine is converted to HCl. A UV-catalyzed experiment of this kind was carried out using effluent MRI 730, and the initial pH of 5.0 decreased to only 4.6 after all the chlorine had been consumed.

A similar experiment was performed in which the pH was maintained using added alkali. The rates of chlorine consumption and organic oxidation were about the same in each experiment and were comparable to those observed using other effluents. Thus, phosphate buffers do not interfere with either the rate or extent of the light-catalyzed chlorine oxidation nor with the analytical procedures employed.

Microanalysis for Chlorine: It was necessary to develop a reliable analysis for chlorine to be applied to very small samples taken from the irradiated cell containing effluent and chlorine. For this purpose a calibration curve was prepared using an orthotolidine-arsenite procedure capable of detecting 1-40 mg/liter of chlorine in 50 μl of sample. The sample (50 μl) was taken from a chlorine solution which had been analyzed amperometrically (4 ml diluted to 200 ml). The sample was mixed with 2.5 ml of orthotolidine reagent (0.0675 g in 500 ml of water; a 1:20 dilution of the conventional reagent) in a 1-cm cylindrical quartz cell and was shaken for exactly 30 sec. At this time, 3 drops of sodium arsenite (5.0 g of $NaAsO_2$ in 1 liter of water) was added, the cell was shaken and the absorbance at 440 mμ (0.01-mm slit width) was determined immediately. A straight line passing through the origin was obtained when the absorbance was plotted *versus* concentration from 0 to 40 mg/liter.

Using this method, the concentration of chlorine was determined at various stages of the effluent oxidation in the irradiated cell.

Effluent-Irradiation Procedure: Each 50-ml portion of effluent was treated with 1.25 g of monopotassium dihydrogen phosphate (KH_2PO_4), 0.025 g of disodium monohydrogen phosphate (Na_2HPO_4) and sufficient chlorine water to produce the desired initial concentration.

Prior to each series of effluent irradiation experiments, the intensity of the radiation incident on the cell was determined using the ferrioxalate actinometer. Each actinometer study consisted of a series of accurately timed irradiation exposures. Two or more exposure times were employed, and, at each time level, duplicate or triplicate runs were made. Care was taken to insure that the actinometer solution was not overexposed.

Total Organic Carbon Determinations: Total organic carbon (TOC) was determined using the Beckman, Model 915, Total Organic Carbon Analyzer.

Experimental Problems: Because the wavelength-effect experiments required small volumes of reaction mixtures, TOC determinations were the only feasible method for determining changes in the organic content of the irradiated effluent. The determination of changes in chlorine concentrations was very precise, but the precision of the TOC determinations was unsatisfactory for small changes in organic concentration. To overcome this problem, critical experiments were repeated until an acceptable degree of confidence in the results could be obtained.

Another factor which influenced the precision of the results is the determination of UV absorbances of irradiated and nonirradiated samples at relatively long wavelengths (350 mμ, and longer). The absorbance figures are required in order to calculate the amount of radiant energy absorbed. Since the absorbance of a chlorinated effluent in a 1-cm cell is relatively low at these wavelengths (absorbance equals approximately 0.04 at 360 mμ), the error inherent in the spectrophotometer (estimated to be about 0.005) becomes very significant.

Experimental Results: The results of monochromatic wavelength-effect experiments are presented in the following paragraphs.

At 366 mμ: The results of the effluent oxidation studies at 366 mμ are presented in Table IV. The actinometer data are presented in Table V, and a description of the effluents used is presented in Table VI. The radiant energy absorbed by the effluent-chlorine solution was calculated from the applied energy (actinometer data), multiplied by the UV absorption (fraction of incident intensity absorbed). The UV absorption was obtained by determining the UV absorption spectrum of the effluent-chlorine solution before and after irradiation. If considerable decrease in absorption occurred, then an average of the absorption before and after irradiation was used.

Except for one, apparently anomalous, result, very little decrease in chlorine concentration or TOC was observed at this wavelength even when the energy absorbed was 23 w min/gal.

At 436 mμ: The results obtained at 436 mμ are presented in Table VII. This wavelength appears to be very ineffective in reducing chlorine concentration or TOC. Because of low absorbance, long irradiation times were required in order to obtain significant energy absorption by the solution.

At 313 mμ: The results obtained at 313 mμ are presented in Table VIII, p. 41. This wavelength is considerably more effective in lowering chlorine concentration and TOC than are longer wavelengths. (The chlorine concentration decreased by 75 mg/liter, but the TOC decreased only 1.9 mg/liter upon the absorption of 29 w min/gal. of radiant energy.)

At 405 mμ: The 405-mμ interference filter used with the high-pressure, PEK, mercury-arc lamp produces adequate monochromatic radiation intensities for the photochemical study (Table V). However, the low absorption of this radiation by the effluent-chlorine mixture (Table IX) results in relatively small amounts of radiant energy absorbed (only 7.7 w min/gal. after 1 hr). Under these conditions, very little decrease in chlorine concentration or TOC was achieved (Table X).

The intensity of 405-mμ radiation impinging on the cell in these experiments is 580 μw/cm^2, a relatively high value (2.2 x 10^3 μw of energy impinge upon the 3.8-cm^2 area of the cell). In order to deliver to the solution an amount of energy equivalent to 15 w min/gal. within 15 min, the intensity of radiation impinging on the cell would have to be increased to about 8 times its present value. In actual practice, incident intensities at 405 mμ of the required magnitude (about 2,000 μm/cm^2) would probably be impractical.

TABLE IV

MONOCHROMATIC WAVELENGTH-EFFECT STUDIES AT 366 mμ[a]

Radiant Energy Entering Cell[b] (mw)	Dark Chlorination Time (hr)	Irradiation Time (min)	Radiant Energy Applied (w min/gal.)	Radiant Energy Absorbed (w min/gal.)	Chlorine Concentration (mg/ℓ)		TOC (mg/ℓ)	
					Before	After	Before	After
3.2	24	10	40.5	3.5	63	62	-	-
3.2	24	20	81.0	7.0	63	58	-	-
3.2	1	10	40.5	3.1	72	63	8.0	8.2
3.2	3	30	122	9.3	71	63	8.0	8.1
1.2	4	30	47	3.8	74	14[c]	7.5	6.8
1.2	1	30	47	3.8	72	64	7.2	7.1
1.2[d]	2	30	9.4	4.2	68	66	7.2	7.1
2.7	48	120	390	17.0	89	65	9.1	7.9
2.7	48	63	205	12.0	89	85	8.8	9.1
2.7	48	60	195	12.0	89	79	8.9	8.7
2.7	72	120	390	23.0	84	71	8.7	9.2

---

[a] All except one of the effluent oxidations were performed using a cylindrical quartz cell, 1 cm in length. The first seven experiments employed effluent MRI 731. The last four employed effluent MRI 925. The characteristics of these effluents are presented in Table VI.

[b] The actinometer results are presented in Table V.

[c] This anomalous result was not confirmed by subsequent experiments.

[d] This experiment was performed using a 5-cm cell.

TABLE V

ACTINOMETRIC CALIBRATION OF RADIATION SOURCES FOR MONOCHROMATIC WAVELENGTH-EFFECT STUDIES

Radiation Source[a]	Radiation Wavelength ($m\mu$)	Exposure Time (sec)	Increase in Absorbance at 510 $m\mu$	Number of Fe^{++} Ions Produced (x 10^{-16})	Radiant Energy Entering Cell	
					(quanta/sec x 10^{-15})	(mw)
A	366	30	0.524	21.3	5.88	3.20
B	366	15	0.102	4.15	2.21	1.21
C	366	15	0.210	8.54	4.85	2.65
A	313	60	0.017	0.69	0.093	0.059
C	313	60	0.396	16.1	2.17	1.37
C	313	60	0.301	12.2	1.65	1.04
C	436	30	0.297	12.1	7.92	3.61
C	405	30	0.310	14.6	4.84	2.37
C	405	60	0.717	29.2	4.82	2.36
C	405	90	1.05	42.7	4.71	2.31
C	546	--	--	--	--	1.8[b]

---

[a] Radiation sources: A, PEK lamp with pyrex lenses; B, same lamp with lenses removed; C, same lamp, no lens, located nearer to filter.

[b] This value was estimated; see text.

TABLE VI

CHARACTERISTICS OF EFFLUENTS USED IN THE MONOCHROMATIC WAVELENGTH-EFFECT STUDIES

	MRI 731[a]	MRI 925
COD (mg/ℓ)	23.6	30
TOC (mg/ℓ)	8.4	10.6
Turbidity (JTU)	1	1.9
Ammonia-N (mg/ℓ)	2.5	0.8
Nitrate-N (mg/ℓ)	22	7.2
Chlorine demand (mg/ℓ)	-	8.3

---

[a] The designation MRI 731 indicates that the effluent was prepared at MRI on July 31 using a laboratory-scale activated sludge facility starting with effluent from the Gracemore (Missouri) Municipal Sewage Treatment Plant.

TABLE VII

MONOCHROMATIC WAVELENGTH-EFFECT STUDIES AT 436 mμ

Radiant Energy Entering Cell (mw)	Dark Chlorination Time (hr)	Irradiation Time (min)	Radiant Energy Applied (w min/gal.)	Radiant Energy Absorbed (w min/gal.)	Chlorine Concentration (mg/ℓ)		TOC (mg/ℓ)	
					Before	After	Before	After
3.61	24	30	136	1.4	140	135	8.1[a]	8.0
3.61	2	30	136	1.4	122	119	10.6[b]	10.3
3.61	4	120	544	5.4	109	108	9.9[b]	10.0

---

a/ Effluent MRI 731.
b/ Effluent MRI 925.

TABLE VIII

MONOCHROMATIC WAVELENGTH-EFFECT STUDIES AT 313 mμ

Radiant Energy Entering Cell (mw)	Dark Chlorination Time (hr)	Irradiation Time (min)	Radiant Energy Applied (w min/gal.)	Radiant Energy Absorbed (w min/gal.)	Chlorine Concentration (mg/ℓ)		TOC (mg/ℓ)	
					Before	After	Before	After
0.059	48	161	11.9	2.9	71	56	--	--
0.059	96	157	11.6	2.3	53	47	8.1[a]	8.5
1.37	1	30	52	10	150	128	8.1[b]	8.2
1.04	1	130	171	29	118	43	8.4[b]	6.5
1.04	24	60	79	13	99	67	8.4[b]	7.4

---

a/ Effluent MRI 731.
b/ Effluent MRI 925.

Furthermore, the data show that, at the presently available intensity, the application of 15-16 w min/gal. in 120-135 min does not produce significant decreases in TOC and does not produce large decreases in chlorine concentration.

TABLE IX

UV-ABSORPTION CHARACTERISTICS OF CHLORINATED EFFLUENTS USED IN MONOCHROMATIC WAVELENGTH-EFFECT STUDIES

	Chlorine Concentration (mg/ℓ)		Absorbance (1-cm cell)		Fraction of Radiation Absorbed	
	Initial	Final	Initial	Final	Initial	Final
At 405 mμ*	84	80	0.021	0.021	0.046	0.046
	109	91	0.021	0.021	0.046	0.046
	112	94	0.021	0.021	0.046	0.046
At 546 mμ*	95	90	0.005	0.005	0.010	0.010

---

* Absorbances were calculated from absorbances determined in a 10-cm cell compared to the absorbance of ultrapure water in the same cell.

At 546 mμ: Additional problems were encountered in determining the usefulness of longer wavelength radiation. The 546-mμ radiation from a mercury arc is absorbed to a much lesser extent by the chlorinated effluent than the 405-mμ radiation. Moreover, the intensity of the 546-mμ radiation cannot be determined by actinometry because the quantum yield at this wavelength for the ferrioxalate actinometer is nearly zero (see Appendix B).

The intensity of radiation at this wavelength can be estimated by comparing the relative intensities of emitted radiation at 405 mμ and 546 mμ and the relative transmission of the two wavelengths by the filters (Table XI). By multiplying the observed intensity at 405 mμ (2.2×10^{-3} w) by the calculated ratio of the energy transmitted by the filters (0.055), an estimate can be obtained for the intensity of 546-mμ radiation impinging on the sample (1.2×10^{-3} w).

TABLE X

MONOCHROMATIC WAVELENGTH-EFFECT STUDIES AT 405 $m\mu$ and 546 $m\mu$[a]

Wavelength ($m\mu$)	Radiant Energy Entering Cell (mw)	Dark Chlorination Time (hr)	Irradiation Time (min)	Radiant Energy Applied (w min/gal.)	Fraction of Radiation Absorbed[b]	Radiant Energy Absorbed (w min/gal.)	Chlorine Concentration (mg/ℓ)		TOC (mg/ℓ)	
							Before	After	Before	After
405	2.2	72	60	167	0.046	7.7	84	80	8.9	9.3
405	2.2	96	120	333	0.046	15.3	109	91	9.9	9.4
405	2.2	1	135	374	0.046	17.2	112	94	8.3	8.3
546	1.2	24	120	180	0.010	1.8	95	90	8.2	8.8

---

a/ All of the effluent oxidations were performed using a cylindrical quartz cell, 1 cm in length. Effluent MRI 925 (Table VI) was used in all of the experiments.

b/ The fraction of radiation absorbed is the average of initial and final values (see Table IX).

TABLE XI

ESTIMATED INTENSITY OF 546-mμ RADIATION TRANSMITTED BY FILTER

Wavelength (mμ)	Irradiated Intensity[a] (mw/steradian)	Fraction Transmitted by Interference Filter[b]	Relative Amount of Radiant Energy Transmitted by Filter (mw/steradian)
405	15	0.37	5.5
546	10	0.30	3.0

---

[a] These values are supplied by the lamp manufacturer, PEK Applications Information Sheet No. AN-202.

[b] The transmission values were obtained experimentally using a Beckman, DK-2, spectrophotometer.

As shown in Table IX, only 1% of the radiation at 546 mμ is absorbed by a 1-cm cell. Thus, although the applied energy was 180 w min/gal. (Table X), the absorbed energy was only 1.8 w min/gal.

The absorption of this amount of energy at this wavelength did not decrease the TOC and only slightly decreased the chlorine concentration. The delivery of more than 1.8 w min/gal. of radiation at this wavelength would probably be impractical.

At 254 mμ: The monochromatic ultraviolet source used in these experiments was the low-pressure, mercury-arc lamp described earlier in this section. The lamp was located at point near the irradiation chamber, and no filter was employed.

Duplicate experiments were run in each series, and corresponding samples were acidified to pH 2, dechlorinated with a slight excess of sodium bisulfite and shipped to the Taft Water Research Center in Cincinnati for TOC analyses. (The Beckman TOC analyzer at MRI was not operating reliably during these experiments.)

A summary of the experimental data is presented in Tables XII to XVI. In general, the decreases in absorbance, chlorine concentration, and TOC were proportional to the radiant energy absorbed.

TABLE XII

MONOCHROMATIC WAVELENGTH-EFFECT STUDIES AT 254 $m\mu$

Irradiation Time (min)	Radiant Energy Absorbed[a] (w min/gal.)	Chlorine Concentration (mg/ℓ) Initial	Final	Difference	TOC[b] (mg/ℓ) Initial	Final	Difference
20	11.8	70.3	42.5	27.8	5.9	5.3	0.6
20	11.8	68.2	41.0	27.2	(9.2)	(9.4)	-0.2
20	12.4	92.3	52.9	39.4	8.9	8.9	0.0
20	12.0	96.4	54.3	42.1	(9.6)	(8.6)	1.0
40	21.3	69.0	21.5	47.5	11.5	7.8	3.7
40	20.1	69.0	21.5	47.5	(9.2)	(7.0)	2.2
40	22.5	89.5	25.7	63.8	8.5	5.9	2.6
40	22.2	88.9	22.7	66.2	(9.2)	(7.8)	1.4
62	32.1	67.8	4.2	63.6	8.8	5.1	3.7
60	32.4	68.9	4.2	64.7	(10.4)	(8.6)	1.8
60	31.6	100.9	9.2	91.7	8.9	5.9	3.0
60	31.2	98.3	10.2	88.1	(11.8)	(7.2)	4.6

---

[a] Data for the calculation of Radiant Energy Absorbed are listed in Table XIV.

[b] The parentheses indicate TOC analyses which were performed at the Robert A. Taft Water Research Center.

TABLE XIII

SUMMARY OF TOC DECREASES AT 254 $m\mu$[a]

	Irradiation Time (min) 20	40	60
TOC Decreases (mg/ℓ)	0.6	3.7	3.7
	-0.2	2.2	1.8
	0.0	2.6	3.0
	1.0	1.4	4.6
Averages	0.4	2.45	3.27

---

[a] The experiments are described in Table XII.

TABLE XIV

RADIANT ENERGY AT 254 mμ ABSORBED BY CHLORINATED EFFLUENTS

Irradiation Time (min)	Radiant Energy Entering Cell[a] (mw)	Radiant Energy Applied (w min/gal.)	Fraction of Energy Absorbed[b]	Radiant Energy Absorbed (w min/gal.)
20	1.15	29.0	0.408	11.8
20	1.15	29.0	0.406	11.8
20	1.15	29.0	0.430	12.4
20	1.15	29.0	0.415	12.0
40	1.15	58.1	0.367	21.3
40	1.15	58.1	0.346	20.1
40	1.15	58.1	0.387	22.5
40	1.15	58.1	0.382	22.2
62	1.15	90.0	0.358	32.1
60	1.15	87.2	0.372	32.4
60	1.15	87.2	0.363	31.6
60	1.15	87.2	0.358	31.2

---

a/ From average of Actinometer Studies, Table XVI.

b/ From UV Absorption Characteristics, Table XV.

TABLE XV

UV-ABSORPTION CHARACTERISTICS OF CHLORINATED EFFLUENTS USED IN 254-mμ WAVELENGTH-EFFECT STUDIES

Irradiation Time (min)	Absorbance (1-cm cell)		Fraction of Radiation Absorbed		
	Initial	Final	Initial	Final	Average
20	0.272	0.188	0.465	0.351	0.408
20	0.263	0.185	0.463	0.348	0.406
20	0.343	0.193	0.500	0.359	0.430
20	0.317	0.182	0.479	0.351	0.415
40	0.260	0.146	0.450	0.284	0.367
40	0.252	0.126	0.440	0.251	0.346
40	0.345	0.140	0.500	0.274	0.387
40	0.320	0.140	0.490	0.274	0.382
62	0.282	0.120	0.476	0.240	0.358
60	0.290	0.129	0.487	0.257	0.372
60	0.307	0.125	0.475	0.250	0.363
60	0.302	0.115	0.484	0.231	0.358

TABLE XVI

ACTINOMETRIC CALIBRATION OF THE RADIATION SOURCE FOR MONOCHROMATIC WAVELENGTH-EFFECT STUDIES AT 254 mμ[a]

Exposure Time (sec)	Increase in Absorbance at 510 mμ	No. of Fe^{++} Ions Produced ($x\ 10^{-16}$)	Radiant Energy Entering Cell (quanta/sec $x\ 10^{-15}$)	(mw)
60	0.271[b]	11.0	1.47	1.15
120	0.572[b]	23.0	1.55	1.21

---

[a] The monochromatic UV source was a low-pressure mercury-arc lamp.

[b] Average of two experiments.

TABLE XVII

SPECTRAL OUTPUT OF MERCURY-ARC SPOTLAMP (100-CH-4, SPOT. H38-4GS)

Wavelength Range (mμ)	Watts Radiated	Fraction of Total Output (F_λ/F) 300-540 mμ	Fraction of Total Output (F_λ/F) 300-550 mμ
300-310	0.01	0.004	0.002
310-320	0.13	0.048	0.030
320-330	0.04	0.015	0.009
330-340	0.09	0.033	0.021
340-350	0.05	0.018	0.012
350-360	0.06	0.022	0.014
360-370	0.16	0.058	0.037
370-380	0.06	0.022	0.014
380-400	0.14	0.051	0.033
400-410	0.55	0.201	0.128
410-430	0.09	0.033	0.021
430-440	1.01	0.369	0.236
440-540	0.35	0.128	0.082
540-550	1.55	--	0.361
550-570	0.14	--	--
570-580	1.53	--	--
580-760	0.96	--	--

The TOC data obtained from the Taft Water Research Center essentially confirmed the TOC data obtained at MRI in duplicate experiments. However, the inherent lack of precision, at this level of TOC difference, was apparent.

Polychromatic Wavelength-Effect Experiments

The effect of the radiation from a polychromatic, mercury-arc lamp on the chlorine oxidation of effluents was investigated. The techniques used were similar to those used in the monochromatic, wavelength-effect studies (1-cm quartz-cell reactors). The spectral ouput of the lamp is presented in Table XVII. (Note that there is no significant emission below 300 mμ.)

Actinometric studies were employed to provide an estimate of the intensity of the radiation entering the cell.

Data required for polychromatic actinometer calculations are presented in Table XVIII. As indicated in Table XVIII, the value of the desired summation is as shown below:

$$\sum_{\lambda} \lambda \, \varphi_{\lambda} \, (1-T)_{\lambda} \, (F_{\lambda}/F_{300-540}) = 322.47$$

Thus, from Eq. (11) derived in the first part of this Experimental section:

$$I_{300-540} = \frac{A_{510}}{t_{sec}} \times 0.251$$

Actinometer data for the mercury-arc spotlamp are presented in Table XIX. The total intensity between 300 mμ and 540 mμ, as calculated according to the above equation, was 3.9×10^{-3} w.

As indicated in Table XVII, there is a certain amount of flexibility in selecting the wavelength range for determining "total" intensity. In our opinion, the wavelengths which must be considered are those which influence the actinometer. Wavelengths which do not affect the actinometer cannot be measured. There are two factors which can influence the extent of actinometer response: the quantum yield and the fraction of the radiation absorbed. For the ferrioxalate actinometer, both the quantum yield and the fraction absorbed become very small at about 540 mμ. (See Table XVIII.) However, there is a very intense mercury emission at 546 mμ. The inclusion of this emission line into the actinometer calculations will affect the

TABLE XVIII

DATA FOR ACTINOMETRIC CALCULATION OF INTENSITY OF MERCURY-ARC SPOTLAMP (WESTINGHOUSE 100-CH-4)

Wavelength (mμ)	Quantum Yield (φ)	Fraction of Radiation Absorbed by Actinometer (1-T)	Fraction of Emitted Radiation Which Affects Actinometer $(F_\lambda/F_{300-540})$	$\lambda\ \varphi_\lambda(1-T)_\lambda\ (F_\lambda/F_{300-540})$
305	1.24	1.00	0.004	1.40
315	1.24	1.00	0.048	18.57
325	1.24	1.00	0.015	5.88
335	1.23	1.00	0.033	13.51
345	1.23	1.00	0.018	7.76
355	1.22	1.00	0.022	9.48
365	1.22	1.00	0.058	25.99
375	1.21	1.00	0.022	9.94
390	1.18	0.99	0.051	23.25
405	1.15	0.95	0.201	89.04
420	1.12	0.81	0.033	12.50
435	1.11	0.56	0.369	99.63
490	0.88	0.10	0.128	5.52
545	0.27	0.01	--	--
				322.47

TABLE XIX

ACTINOMETER DATA FOR MERCURY-ARC SPOTLAMP (100-CH-4)

Exposure Time (sec)	A_{510} a/
30	0.452
30	0.447
30	0.497
15	0.217
15	0.239
15	0.248

---

a/ A_{510} is the difference in absorbance, at 510 mμ, between the exposed and nonirradiated actinometer solutions.

calculated fraction of total output (F_λ/F_{tot}) and the calculation of total intensity. However, the "total" intensity can be calculated with or without this wavelength because of its relatively small effect on the actinometer solution. Because of this flexibility, it is necessary to distinguish exactly which wavelength range constitutes the "total" energy output.

Results of the effluent irradiation experiments employing polychromatic radiation are presented in Table XX. Note that the applied intensities are very large compared to those used in the monochromatic, wavelength-effect experiments.

The calculation of total energy absorbed would require determination of the fraction of energy absorbed at each wavelength. The longer wavelengths, 400 mμ and above, are only slightly absorbed, and spectrophotometer data obtained using longer cells would be required in order to obtain absorption data sufficiently precise to carry out this calculation.

Wavelengths above 400 mμ represent a very large portion (about 73%) of the "total" radiant energy applied, but this energy is almost completely wasted because of the low absorption. Wavelengths below 400 mμ are much more strongly absorbed, and an estimate of the amount of energy absorbed between 300-370 mμ is presented in Table XXI.

A number of significant facts are apparent from a consideration of Tables XX and XXI. First, of the total of over 7,000 w min/gal. of applied radiant energy, only a small fraction, about 140 w min/gal., is absorbed. Second, the major fraction of energy which is absorbed is in the wavelength range of 300-370 mμ, and energy absorbed in this range does not produce the extent of oxidation which can be achieved at lower wavelengths. The results of these experiments confirm the results of the monochromatic, wavelength-effect experiments.

Intensity-Time Experiments

The intensity-time experiments were performed using the same equipment used in the wavelength-effect studies. The ultraviolet source, however, was the unfiltered radiation from a low-pressure, mercury-arc lamp.

Data supplied by the manufacturer (Nester-Faust) indicate that 96% of the UV output of this lamp is between 245 mμ and 260 mμ.

In the first series of experiments, the intensity of the radiant energy and the irradiation time were varied. Particular attention was paid to experiments in which the product of intensity and time was constant. The results are presented in Tables XXII-XXVI.

TABLE XX

RESULTS OF POLYCHROMATIC WAVELENGTH-EFFECT EXPERIMENTS

Run No.	Intensity[a] (w)	Irradiation Time (min)	Total Radiant Energy Applied[b] (w min/gal.)	Chlorine Concentration (mg/ℓ) Initial	Chlorine Concentration (mg/ℓ) Final	Chlorine Concentration (mg/ℓ) Difference	TOC (mg/ℓ) Initial	TOC (mg/ℓ) Final	TOC (mg/ℓ) Difference
45-1	0.164	5.0	1,040	138	111	27	9.8	8.6	1.2
45-3	0.192	15.0	3,600	136	83	53	8.6	7.9	0.7
47-1	0.187	30.0	7,050	138	60	78	7.9	5.5	2.4

---

a/ The UV source was a Westinghouse (100-CH-4) spotlamp.

b/ These figures show the total applied energy within the wavelength range, 300-540 mμ.

TABLE XXI

ESTIMATION OF ABSORPTION OF POLYCHROMATIC RADIATION BY CHLORINATED EFFLUENT (RUN 47-1, TABLE XX)

Wavelength Range (mμ)	Fraction of Total Emitted Radiation	Radiant Energy Entering Cell[a] (w)	Fraction of Radiant Energy Absorbed[b] (w)	Energy Absorbed (w min/gal.)
300-310	0.004	0.00076	0.250	7.2
310-320	0.048	0.00912	0.190	65.5
320-330	0.015	0.00285	0.150	16.2
330-340	0.033	0.00627	0.010	2.4
340-350	0.018	0.00342	0.090	11.6
350-360	0.022	0.00418	0.065	10.3
360-370	0.058	0.01100	0.065	27.1
				140.3

---

a/ The radiant energy entering cell is calculated by multiplying the "total" intensity obtained from the actinometer data (0.19 w.) by the fraction of total radiation emitted within the particular wavelength range.

b/ As before, these values are obtained from the UV-absorption curves. Estimates were required in some cases because of the low absorption by 1-cm. cells.

TABLE XXII

INTENSITY-TIME STUDIES (FIRST SERIES)

Run No.	Intensity (mw)	Irradiation Time (min)	Radiant Energy Absorbed[a] (w min/gal.)	Chlorine Concentration (mg/ℓ) Initial	Final	Difference	Absorbance Decrease[b] ΔA_T	ΔA_{Cl_2}	ΔA_{Eff}
1	3.07	7.4	28.6	68.4	42.1	26.3	0.122	0.027	0.095
2	3.07	7.4	28.6	56.4	25.7	30.7	0.119	0.032	0.087
3	3.07	14.8	57.1	54.8	13.6	41.2	0.120	0.042	0.078
4	3.07	14.8	57.1	52.2	-	-	0.120	-	-
5	3.07	14.8	57.1	96.4	9.3	87.1	0.208	0.088	0.122
6	3.07	7.4	28.6	59.3	29.7	29.1	0.141	0.031	0.110
7	3.07	7.4	28.6	94.1	53.6	40.5	0.141	0.041	0.100
8	1.34	16.9	28.6	72.0	38.0	34.0	0.090	0.035	0.055
9	1.34	16.9	28.6	105.0	58.0	47.0	0.113	0.048	0.065
10	1.34	16.9	28.6	93.8	53.5	40.3	0.097	0.041	0.056
11	0.94	24.3	28.6	90.9	52.5	38.4	0.080	0.039	0.041

---

a/ Data for the calculation of Radiant Energy Absorbed are listed in Table XXIII.

b/ Absorbance decrease; ΔA_T = total observed decrease in absorbance
ΔA_{Cl_2} = absorbance decrease attributable to decrease in chlorine concentration
ΔA_{Eff} = absorbance decrease attributable to decrease in absorbance of effluent.
$(\Delta A_T = \Delta A_{Cl_2} + \Delta A_{Eff})$

TABLE XXIII

RADIANT ENERGY ABSORBED (FIRST INTENSITY-TIME SERIES)

Run No.	Irradiation Time (min)	Radiant Energy Entering Cell[a] (mw)	Radiant Energy Applied (w min/gal.)	Fraction of Energy Absorbed[b]	Radiant Energy Absorbed (w min/gal.)
1	7.4	3.07	28.6	0.434	12.4
2	7.4	3.07	28.6	0.413	11.8
3	14.8	3.07	57.1	0.339	19.4
4	14.8	3.07	57.1	0.348	19.9
5	14.8	3.07	57.1	0.425	24.3
6	7.4	3.07	28.6	0.423	12.1
7	7.4	3.07	28.6	0.446	12.8
8	16.9	1.34	28.6	0.330	9.44
9	16.9	1.34	28.6	0.363	10.4
10	16.9	1.34	28.6	0.346	9.90
11	24.3	0.94	28.6	0.328	9.38

---

[a] From average of Actinometer Studies, Table XXV.

[b] From UV-Absorption Characteristics, Table XXIV.

TABLE XXIV

UV-ABSORPTION CHARACTERISTICS OF CHLORINATED EFFLUENTS (FIRST INTENSITY-TIME SERIES)

Run No.	Absorbance (1-cm cell) Initial	Absorbance (1-cm cell) Final	Fraction of Radiation Absorbed Initial	Fraction of Radiation Absorbed Final	Fraction of Radiation Absorbed Average
1	0.313	0.191	0.512	0.355	0.434
2	0.296	0.177	0.492	0.334	0.413
3	0.244	0.124	0.429	0.248	0.339
4	0.250	0.130	0.438	0.258	0.348
5	0.356	0.148	0.559	0.290	0.425
6	0.316	0.175	0.516	0.330	0.423
7	0.333	0.192	0.535	0.356	0.446
8	0.222	0.132	0.400	0.260	0.330
9	0.257	0.144	0.446	0.280	0.363
10	0.236	0.139	0.419	0.273	0.346
11	0.215	0.135	0.390	0.266	0.328

TABLE XXV

ACTINOMETRIC CALIBRATION[a] (FIRST INTENSITY-TIME SERIES)

Exposure Time (sec)	Increase in Absorbance at 510 $m\mu$	Radiant Energy Entering Cell (mw)
20	0.235	3.00
20	0.245	3.13
30	0.458	3.91
30	0.278	2.36
30	0.255	2.51
30	0.166	1.38
30	0.169	1.40
30	0.162	1.35
120	0.635	1.36
120	0.619	1.32
60	0.384	1.63
60	0.252	1.09
60	0.232	0.98

---

[a] The Monochromatic UV-source was a low-pressure, mercury-arc lamp.

TABLE XXVI

A COMPARISON OF EFFLUENTS MRI 925 AND MRI 112

	MRI 925[a]	MRI 112
COD (mg/ℓ)	29.1 (30.0)	18.4
TOC (mg/ℓ)	- (10.6)	11.0
Turbidity (JTU)	0.95 (1.9)	1.0
Ammonia-N (mg/ℓ)	0.2 (0.8)	0.1
Nitrate-N (mg/ℓ)	5.0 (7.2)	27.0
Chlorine Demand (mg/ℓ)	8.9 (8.3)	3.6

---

[a] Figures in parentheses are data obtained when the effluent was fresh.

Complete data could not be obtained because of a breakdown in the TOC analyzer. However, the preliminary conclusion (Table XXII) was that the extent of reaction as measured by the decrease in chlorine concentration and the decrease in effluent absorbance is not proportional to the product of intensity and time. That is, at a given level of absorbed energy, low intensities appear to produce greater decreases in chlorine concentration and absorbance.

The second series of experiments was performed using a freshly prepared effluent (MRI 112). This effluent was very similar to the effluent used in the first series (MRI 925). Analytical comparisons and oxidation characteristics are presented in Tables XXVI and XXVII.

TABLE XXVII

A COMPARISON OF THE UV-CHLORINE OXIDATION CHARACTERISTICS OF EFFLUENTS MRI 925 AND MRI 112[a]

	Before Irradiation	After Irradiation
MRI 925		
TOC (mg/ℓ)	9.1	6.6
Cl_2 (mg/ℓ)	79.0	2.5
UV absorbance (254 mμ, 1-cm cell, versus air)	0.220	0.084
MRI 112		
TOC (mg/ℓ)	10.8	7.8
Cl_2 (mg/ℓ)	79.0	8.5
UV absorbance (254 mμ, 1-cm cell, versus air)	0.265	0.120

---

[a] Reaction conditions: Effluents buffered to pH 5.0; 1-cm quartz cell; source, low-pressure mercury-arc lamp (254 mμ); intensity 3 mw; irradiation time, 30 min.

The results of the second series of intensity-time experiments are summarized in Tables XXVIII-XXX. Experimental procedures were the same as in the first series.

TABLE XXVIII

INTENSITY-TIME STUDIES (SECOND SERIES)

Run No.	Irradiation Time[a] (min)	Intensity[b] (mw)	Radiant Energy Absorbed[c] (w min/gal.)	Chlorine Concentration (mg/ℓ)			TOC (mg/ℓ)				Absorbance Decrease[d]		
				Initial	Final	Difference	Initial	Final	Difference	(%)	ΔA_T	ΔA_{Cl_2}	ΔA_{Eff}
32-1	15.0	3.0	22.5	106	42	64	9.6	7.0	2.6	27	0.138	0.083	0.055
32-3	7.5	3.0	15.2	105	65	40	9.6	8.5	1.1	12	0.100	0.062	0.038
32-5	15.0	3.0	21.5	105	43	62	8.8	7.8	1.0	10	0.113	0.082	0.031
32-7	30.0	2.0	28.1	100	24	76	8.5	6.9	1.6	19	0.135	0.093	0.042
32-9	15.0	2.0	14.8	101	48	53	8.1	7.1	1.0	12	0.090	0.073	0.017
32-11	30.0	1.0	14.9	106	50	56	9.3	8.3	1.0	11	0.135	0.076	0.059
32-15	60.0	1.0	27.1	99	20	79	9.1	5.3	3.8	42	0.148	0.096	0.052
36-1	50.0	3.0	77.1	145	7	138	10.3	4.5	5.8	56	0.153	0.148	0.005
36-3	88.0	3.0	122.0	143	0	143	9.1	3.2	6.9	76	0.181	0.153	0.028
36-5	26.0	3.0	38.2	136	31	105	8.7	5.2	3.5	40	0.141	0.119	0.022
36-7	50.0	2.0	45.0	139	18	121	8.4	6.9	1.5	18	0.171	0.134	0.037
36-9	101.0	2.0	96.4	142	3	139	10.4	5.5	4.9	47	0.192	0.149	0.043

---

a/ The effluent used in these studies was MRI 112. The properties of this effluent are compared to the effluent used in past experiments (MRI 925; Tables XXVI and XXVII).

b/ The source was an unfiltered, low-pressure, mercury-arc lamp.

c/ Data for the calculation of radiant energy absorbed are presented in Table XXIX.

d/ Absorbance decrease; ΔA_T = total observed decrease in absorbance
ΔA_{Cl_2} = absorbance decrease attributable to decrease in chlorine concentration
ΔA_{Eff} = absorbance decrease attributable to decrease in absorbance of effluent

$$(\Delta A_T = \Delta A_{Cl_2} + \Delta A_{Eff})$$

TABLE XXIX

RADIANT ENERGY ABSORBED (SECOND INTENSITY-TIME SERIES)

Run No.	Irradiation Time (min)	Radiant Energy[a] Entering Cell (mw)	Radiant Energy Applied (w min/gal.)	Fraction of Energy Absorbed[b]	Radiant Energy Absorbed (w min/gal.)
32-1	15.0	3.0	56.7	0.397	22.5
32-3	7.5	3.0	37.8	0.402	15.2
32-5	15.0	3.0	56.7	0.380	21.5
32-7	30.0	2.0	75.6	0.372	28.1
32-9	15.0	2.0	37.8	0.391	14.8
32-11	30.0	1.0	37.8	0.394	14.9
32-15	60.0	1.0	75.6	0.358	27.1
36-1	50.0	3.0	189.0	0.408	77.1
36-3	88.0	3.0	333.0	0.365	122.0
36-5	26.0	3.0	98.2	0.389	38.2
36-7	50.0	2.0	126.0	0.357	45.0
36-9	101.0	2.0	255.0	0.378	96.4

[a] Source was an unfiltered, low-pressure mercury-arc lamp.

[b] From UV-Absorption Characteristics, Table XXX.

TABLE XXX

UV-ABSORPTION CHARACTERISTICS OF CHLORINATED EFFLUENTS (SECOND INTENSITY-TIME SERIES)

Run No.	Absorbance (1-cm cell) Initial	Absorbance (1-cm cell) Final	Fraction of Radiation Absorbed (254 mμ) Initial	Fraction of Radiation Absorbed (254 mμ) Final	Fraction of Radiation Absorbed (254 mμ) Average
32-1	0.295	0.157	0.491	0.302	0.397
32-3	0.277	0.177	0.470	0.334	0.402
32-5	0.268	0.155	0.460	0.300	0.380
32-7	0.275	0.140	0.469	0.274	0.372
32-9	0.263	0.173	0.454	0.327	0.391
32-11	0.290	0.155	0.487	0.300	0.394
32-15	0.273	0.125	0.466	0.250	0.358
36-1	0.310	0.147	0.510	0.305	0.408
36-3	0.297	0.116	0.495	0.235	0.365
36-5	0.289	0.148	0.487	0.290	0.389
36-7	0.285	0.114	0.481	0.232	0.357
36-9	0.313	0.121	0.514	0.242	0.378

The amount of chlorine consumed was directly proportional to the amount of radiant energy absorbed regardless of the intensity (see Figure 3, p. 10). However, at absorbed energies greater than about 50 w min/gal., the consumption of chlorine did not increase as rapidly with increased energy absorbed (note that in the experiments in which the absorbed energy was more than 50 w min/gal., practically all of the chlorine had been consumed (Table XXVIII)).

The extent of TOC decrease appears to be dependent upon intensity as well as upon energy absorbed. Analysis of the TOC data (Table XXVIII) indicated that, for a given amount of absorbed energy, an intensity of 3 mw was more effective than an intensity of 2 mw, but 1 mw was more effective that 3 mw.

The results of the second series show that there is apparently no relationship between the radiant energy absorbed and the decrease in effluent absorbance.

A third series of experiments was performed to confirm the observation that decreases in TOC were dependent upon intensity, as well as upon total energy absorbed. The results of these experiments are shown in Tables XXXI-XXXIII and are presented graphically in Figure 2, p. 8.

The results confirm that, for a selected quantity of absorbed energy, lower intensities are more effective. However, the difference in effectiveness was not as great as was indicated in the second series of experiments.

As indicated in Figure 2, p. 8, there was almost no intensity effect up to a total absorbed energy of 30 w min/gal. Beyond this level, the lower intensity (1 mw) was significantly more effective than the high intensity (3 mw).

Oxygen-Effect Experiments

The equipment used in these experiments was that used in the original UV-chlorine work; a 5-liter flask was equipped with a quartz immersion well, high-pressure mercury arc, pH electrode, etc. The equipment was described in detail on p. 89 in the Final Summary Report for FWPCA Contract No. 14-12-72. The amount of chlorine used in these experiments was 30% in excess of the stoichiometric amount. In the first series, the chlorine was added at the beginning of the experiment; in the second series, the chlorine was added incremently during the irradiation. The warmed-up lamp was inserted about 1.5 min after the initial quantity of chlorine

TABLE XXXI

INTENSITY-TIME STUDIES (THIRD SERIES)

Run No.	Irradiation Time[a] (min)	Intensity[b] (mw)	Radiant Energy Absorbed[c] (w min/gal.)	Chlorine Concentration (mg/ℓ)			TOC (mg/ℓ)				Absorbance Decrease[d]		
				Initial	Final	Difference	Initial	Final	Difference	(%)	ΔA_T	ΔA_{Cl_2}	ΔA_{Eff}
38-1	20	3.0	33.5	163	54	109	10.1	7.0	3.1	32	0.153	0.107	0.046
38-3	60	1.0	32.8	163	53	110	9.1	5.9	3.2	35	0.134	0.108	0.026
38-5	140	1.0	72.2	163	16	147	9.0	4.2	4.8	53	0.160	0.145	0.015
38-7	47	3.0	66.5	156	15	141	8.4	4.7	3.7	44	0.196	0.140	0.056

---

[a] The effluent used in these studies was MRI 112.

[b] The source was an unfiltered, low-pressure, mercury-arc lamp.

[c] Data for the calculation of radiant energy absorbed are presented in Table XXXII.

[d] Absorbance decrease; ΔA_T = total observed decrease in absorbance
ΔA_{Cl_2} = absorbance decrease attributable to decrease in chlorine concentration
ΔA_{Eff} = absorbance decrease attributable to decrease in absorbance of effluent

$$(\Delta A_T = \Delta A_{Cl_2} + \Delta A_{Eff})$$

TABLE XXXII

RADIANT ENERGY ABSORBED (THIRD INTENSITY-TIME SERIES)

Run No.	Irradiation Time (min)	Radiant Energy[a] Entering Cell (mw)	Radiant Energy Applied (w min/gal.)	Fraction of Energy Absorbed[b]	Radiant Energy Absorbed (w min/gal.)
38-1	20	3.0	75.6	0.443	33.5
38-3	60	1.0	75.6	0.434	32.8
38-5	140	1.0	177	0.408	72.2
38-7	47	3.0	178	0.376	66.5

---

a/ Source was an unfiltered, low-pressure, mercury-arc lamp.
b/ From UV-Absorption Characteristics, Table XXXIII.

TABLE XXXIII

UV-ABSORPTION CHARACTERISTICS OF CHLORINATED EFFLUENTS (THIRD INTENSITY-TIME SERIES)

Run No.	Absorbance (1-cm cell)		Fraction of Radiation Absorbed (253.7 mμ)		
	Initial	Final	Initial	Final	Average
38-1	0.338	0.185	0.540	0.345	0.443
38-3	0.320	0.186	0.520	0.347	0.434
38-5	0.316	0.156	0.516	0.300	0.408
38-7	0.314	0.118	0.513	0.238	0.376

was added, and the total irradiation time was 20 min. The pH was maintained in the range 5.0 to 6.0, and the chlorine concentration was monitored at 3- to 5-min intervals.

The first series of experiments was performed using effluent S&L 527 (the characteristics of this effluent are presented in Table XXXIV). Little difference in oxidation rate was observed in three experiments in which, prior to oxidation, the effluent was (1) purged with nitrogen, (2) purged with oxygen, and (3) given no preliminary treatment. However, rather poor reduction in COD was achieved (a 40% decrease after 10 min in the dark and 7 min irradiation), and the effluent was shown to have an unusually high, initial, chlorine demand (Table XXXIV).

The experiments were repeated using effluent S&L 619, and the results (Table XXXV) were about the same. The extent of oxidation after 10 min in the dark and 7 min irradiation was not as extensive as might be expected.

During this period, the available effluents were low in organic content because the influent was diluted by heavy rains. Considerably lower organic contents were observed, although the ammonia contents were usually low. (See S&L 619 to S&L 729, Table XXXIV.)

At this point, a sample of sludge and a sample of effluent (G 718) were obtained from the Gracemore plant. After the sludge sample had been aerated for 24 hr, the Gracemore effluent was run through the lab-scale digester. As shown in Table XXXIV, the resulting effluents (MRI 720, 726, 731, 804 and 806) were of high quality.

Effluent MRI 720 was used in the final series of oxygen-effect experiments. The results of these experiments are in Table XXXVI and clearly show that there is no significant oxygen effect. Samples for COD and TOC determinations were taken every 5 min, and plots of COD and TOC decrease versus time were almost identical for each experiment.

Batch-Recycle Reactor Experiments

Description of Batch-Recycle Reactor: A diagram of the batch-recycle reactor is presented in Figure 6, p. 15. The reactor portion consisted of a 250-ml, photochemical reaction vessel (Ace Glass, Inc.). A water-cooled, quartz immersion well was placed in the reactor by utilizing the 60/50 glass joint at the top of the reactor. Reactant liquid was pumped into the bottom of the reactor, up past the irradiated zone and back to the reservoir through an outlet near the top of the reactor. A Teflon-clad magnetic stir-bar was located at the bottom of the irradiated zone. The apparatus was constructed in such a manner that the chlorinated effluent would not contact any material except glass or Teflon.

The total volume of liquid in the reactor zone was 288 ml. The irradiated zone was an annular volume, 0.57 cm in thickness and 18 cm in length.

The recycle pump was an all-Teflon Saturn pump (The Fluorocarbon Company) equipped with a Teflon throttling valve.

The reservoir was a 5-liter, four-necked, Pyrex flask equipped with graduated addition funnels for addition of chlorine water and sodium hydroxide. A combination pH electrode was also placed in the reservoir, and

TABLE XXXIV

ANALYTICAL DATA FOR EFFLUENTS USED IN OXYGEN-FFFECT STUDIES

Effluent[a]	COD (mg/ℓ)	TOC (mg/ℓ)	NH_3-N (mg/ℓ)	NO_3-N (mg/ℓ)	Turbidity[b] (JTU) Filtered	Turbidity[b] (JTU) Unfiltered	Initial Chlorine Demand[c] (mg/ℓ)
S&L 527	24.2	8.2	5.3	9.6	1.0	15.0	20.8
S&L 619	17.0	5.8	3.2	10.7	0.7	0.75	2.7
S&L 703	12.6	5.0	--	--	0.63	1.20	1.6
S&L 716	13.6	5.5	--	0.5	0.85	1.10	--
S&L 717	14.1	7.5	11.0	--	0.92	1.95	4.8
G 718	--	27.4	17.0	--	--	--	--
MRI 720	30.7	12.0	2.0	14.0	0.95	--	6.7
MRI 726	27.2	12.6	1.0	28.0	--	--	--
S&L 729	15.7	6.5	--	--	--	--	--
MRI 731	23.6	8.8	2.5	22.0	1.0	--	--
MRI 804	22.9	8.8	1.0	18.5	--	--	2.3
MRI 808	--	--	1.5	--	--	--	4.5

---

a/ The initials "S&L," "G" and "MRI" stand for, respectively, Smith and Loveless, Gracemore and Midwest Research Institute. The S&L effluents are from the Smith and Loveless research site where the influent is sewage from the city of Lenexa. The Gracemore effluents are from the Gracemore sewage treatment plant. The MRI effluents were prepared in a lab-scale, sewage-treatment facility starting with Gracemore effluents. The numbers following the initials refer to the date obtained.

b/ Turbidities were determined using the Hach, Model 2100, Turbidimeter.

c/ Initial chlorine demand was determined by adding chlorine to samples of effluent sufficient to bring the chlorine concentration to about 50 mg/ℓ. A similar determination was made using distilled water as a blank. After 10 min, the difference in chlorine consumed represented the chlorine demand of the effluent.

TABLE XXXV

RESULTS OF FIRST SERIES OF OXYGEN-EFFECT EXPERIMENTS, EFFLUENT (S&L 619)

	COD (mg/ℓ)			TOC (mg/ℓ)		
Effluent Treatment[a]	Initial	Final	% Decrease	Initial	Final	% Decrease
Purged with oxygen	16.0	6.2	61	7.3	4.6	37
Purged with nitrogen	16.6	7.2	57	6.9	3.6	48
No treatment	15.6	6.8	56	6.9	4.2	39

[a] Analytical data for effluent S&L 619 are presented in Table XXXIV.

TABLE XXXVI

RESULTS OF SECOND SERIES OF OXYGEN-EFFECT EXPERIMENTS, EFFLUENT (MRI 720)

	COD (mg/ℓ)			TOC (mg/ℓ)		
Effluent Treatment[a]	Initial	Final	% Decrease	Initial	Final	% Decrease
Purged with oxygen	29.4	4.7	84	12.0	3.1	74
Purged with nitrogen	29.8	3.9	87	12.9	3.4	74
No treatment	30.2	4.4	85	11.8	2.2	81

[a] Analytical data for effluent MRI 720 are presented in Table XXXIV.

a glass tube was used to siphon samples as needed. The liquid in the reservoir was stirred by means of a magnetic stirrer.

Liquid was pumped from the reservoir through a calibrated flowmeter (100-850 ml/min) to the irradiated zone. The flowrate was controlled by means of an all-Teflon throttle valve. A Teflon sample-valve was located in the line from the pump to the irradiated zone.

The UV source was a Nester-Faust, low-pressure, mercury-arc lamp. Data supplied by the manufacturer indicate that 96% of the UV output of this lamp is between 245 mμ and 260 mμ. The maximum electrical input is 50 w, and the lamp is reported to be 80% efficient. According to the manufacturer, the UV output should be about 40 w. However, our actinometer studies (described below) indicated that the UV output was far below this amount, and an explanation is presented later in this section.

An ultraviolet intensity meter was attached to the outer wall of the reactor for the purpose of detecting accidental changes in source intensity. Absolute intensities were determined by actinometric procedures described below.

Batch-Recycle Reactor Procedures: The experimental procedure employed in the recycle reactor studies was as follows. The reservoir (the 5-liter flask) was charged with 5.0 liters of effluent. The low-pressure, mercury-arc source was allowed to warm up for 10 min, and chlorine was added to the reservoir to bring the chlorine concentration to the desired level (5 to 10 mg/liter). The pH was adjusted, if necessary, to about 5.0 using concentrated hydrochloric acid or 10% sodium hydroxide. A sample of the starting mixture was taken, and a UV spectrum (5-cm cell) was obtained. The TOC content of the sample was determined, and the sample was then acidified (1 ml concentrated H_2SO_4/150 ml) and dechlorinated using a stream of nitrogen gas. The COD of the dechlorinated sample was obtained.

The pump was started, and the flow rate was set by adjusting the throttle valve. The sensing portion of the UV meter was attached to the outer wall of the reactor and provided a means for determining whether or not large changes in intensity occurred. Chlorine concentration, pH, flowrate and intensity were monitored frequently during the run. Additional chlorine and sodium hydroxide were added as needed.

The contact time was determined by multiplying the contact time per pass (reactor volume divided by flowrate) by the number of times the reaction mixture was passed through the reactor.

Determination of Fraction of Radiation Absorbed: A critical parameter that required determination was the fraction of radiation absorbed by the chlorinated effluent in the irradiated zone. The UV spectrum of each sample was taken, prior to dechlorination, using 5-cm quartz cells. The observed absorbances at 254 mμ were in the range, 0.571 to 0.120. The first two figures of these absorbance values are highly reliable, but the third figure must be estimated (the chart paper range is 0 to 1.000). The absorbances were run *versus* air using a Beckman DK-1 spectrophotometer. The 5-cm cell was filled with distilled water, and this absorbance was determined during each series of spectrum determinations for the purposes of (1) obtaining a correction factor for cell characteristics (reflection, refraction, etc.) and (2) providing a check on the optical cleanliness of the cell. It is felt that this procedure was less susceptible to error than the procedure of using two matched cells with distilled water in the reference cell. Experience has shown that the spectrum of our distilled water is usually comparable to "ultrapure" water in the wavelength range 250-360 mμ. If the distilled water produced an absorbance higher (at 254 mμ) than expected for "ultrapure" water (0.041), then a check was made on both the purity of the water and the optical quality of the cell.

An additional, somewhat unique, factor required consideration in these determinations: the actual absorbance of pure water. Subtraction of the absorbance of a cell containing distilled water from the absorbance of a cell containing effluent not only corrects for the cell characteristics, but also subtracts the absorbance of pure water. In ordinary UV-spectrum determinations, this produces no problem. However, at 254 mμ, the absorbance by water itself is not negligible ($A = 0.0225$ for a 5-cm thickness)3/ and must be added to the observed absorbance to obtain the absolute absorbance of effluent, plus water. When the absolute absorbance of the 5-cm thickness of chlorinated effluent is obtained, this absorbance is converted by direct proportionality to the absorbance of the 0.57-cm thickness of the irradiated zone of the reactor. This final absorbance is then converted to fraction absorbed (1-T, where T = transmittance) using the equation: $A = \log_{10} 1/T$. This procedure yields highly accurate values for the fraction or radiation absorbed by the chlorinated effluent in the irradiated zone.

Actinometric Determination of Intensity of Low-Pressure Lamp: The reactor portion of the batch-recycle reactor was transferred to a darkroom and filled with actinometer solution [0.006 M $K_3Fe(C_2O_4)_3$] to the same liquid level that would be used in the effluent-oxidation experiments.

The low-pressure mercury-arc lamp, described above, was placed in a cylindrical light-shield and allowed to equilibrate for at least 10 min, during which time cooling air was ciruclated through the shield. Shorter equilibration times produced erratic results. If the lamp was not cooled by air during the equilibration period, the surface temperature of the lamp increased. When the lamp was placed in the reactor, it then cooled causing the emission of varying amounts of UV radiation. (The effect of surface temperature on the emission of low-pressure lamps is well known.)

When the lamp was emitting maximum intensity (at room temperature), it was quickly transferred from the shield to the immersion well. The time period between lamp-in and lamp-off was carefully measured. At the end of the irradiation period, the actinometer solution was drained from the reactor and an aliquot was taken and analyzed for ferrous ion, as in the actinometer experiments. (See Actinometer Procedures, p. 30.)

The results of the reactor actinometer studies are presented in Table XXXVII. The observed intensities were unexpectedly low. This lamp was originally believed to have a total output of 40 w of UV radiation (see Final Summary Report for FWPCA Contract No. 14-12-72, pp. 61 and 92). When the lamp is placed within the immersion well, practically all of the emitted radiation is "trapped" by the reactor zone because 100% of the incident radiation is absorbed by the actinometer solution. Only a small fraction of the emitted radiation from the top of the lamp is lost through the

TABLE XXXVII

ACTINOMETRIC CALIBRATION OF LOW-PRESSURE, MERCURY-ARC LAMP

Dial Setting[a]	Exposure Time (sec)	Absorbance[b]	Absorbance Produced per Second of Exposure	Intensity[c] (w)
High	5.3	0.385	0.0726	1.76
High	5.2	0.370	0.0712	1.72
High	5.7	0.410	0.0719	1.74
High	5.5	0.385	0.070	1.70
Medium	10.4	0.432	0.0415	1.01
Medium	10.2	0.445	0.0436	1.06
Medium	10.4	0.445	0.0428	1.04
Low	32.6	0.780	0.0239	0.579
Low	30.1	0.651	0.0218	0.528
Low	15.5	0.340	0.0219	0.530
Low	15.4	0.325	0.0211	0.511
Low	33.2	0.720	0.0217	0.525
Low	30.1	0.595	0.0198	0.479

---

[a] "High" intensity was produced with the power-supply dial-setting at the maximum (100); "medium" intensity was equivalent to a dial setting of 75; "low" corresponded to a dial setting of 50.

[b] The absorbance figures are the differences between the exposed and non-exposed actinometer solution.

[c] The intensity is the total intensity just outside the quartz immersion well.

upper portion of the reactor. The observed low intensity could not have been caused by deposits on the lamp or on the immersion well because these had been carefully cleaned with concentrated hydrochloric acid. Two possible explanations for the low absorbance are (1) a decrease in the transmission properties of either the lamp or the immersion well, or (2) a decrease in the actual production of UV radiation by the lamp.

Decreases in the UV transmission of glass are produced by a well-known phenomenon called "solarization." Since the immersion well was almost new, its transmission should have been nearly maximum. A consultation with the manufacturer of the lamp (Nester-Faust, Newark, Delaware) revealed that other investigators had observed that the emitted UV radiation from this lamp gradually decreases "to almost zero" because of solarization.

The manufacturer suggests that the intensity can be restored by an annealing process at 550°C. However, this source had been carefully calibrated; therefore, the reactor studies were continued.

The actinometer data almost certainly represented the actual output of the lamp. Additional evidence was available from earlier actinometer studies in which the actinometer solution was placed in 1-cm quartz cells. If the observed intensity is divided by the area of the cell, and if this intensity-per-unit-area is used to calculate the total intensity impinging on a cylindrical surface (whose radius is equal to the cell-to-source distance), a comparable value for the total intensity is obtained.

Experimental Results: The results of the batch-recycle reactor experiments are presented in Figures 9-20 (pp. 68-79) and in Table II (p. 16).

The results of the preliminary investigation of minimum chlorine requirements are presented in Table XXXVIII.

TABLE XXXVIII

RESULTS OF INVESTIGATION OF MINIMUM CHLORINE REQUIREMENT

Run No.[a]	Effluent	COD Decrease[b] (mg/ℓ/min)	TOC Decrease[b] (mg/ℓ/min)	Chlorine[c] Consumed (percent of theoretical)
128	519	0.81	0.24	87
132[a]	519	0.83	0.24	87
201	519	1.39	0.36	[d]
206	623	0.72	0.24	67
210	623	1.10	0.49	[d]

---

[a] In all the runs except Run No. 132, oxygen was bubbled continuously into the reaction mixture. The low-pressure, mercury-arc source was operated at maximum intensity (1.78 w).

[b] The rate of decrease in COD and TOC was calculated as mg/ℓ/min of UV contact time.

[c] The amount of chlorine consumed was calculated as the percent of the stoichiometric amount required to accomplish the observed COD decrease. The stoichiometric amount of chlorine is calculated by multiplying the COD decrease (mg/ℓ) by 4.43.

[d] In Runs 201 and 210, the chlorine concentration was maintained in the range 5-10 mg/ℓ, but no measure of the total amount of chlorine consumed was available.

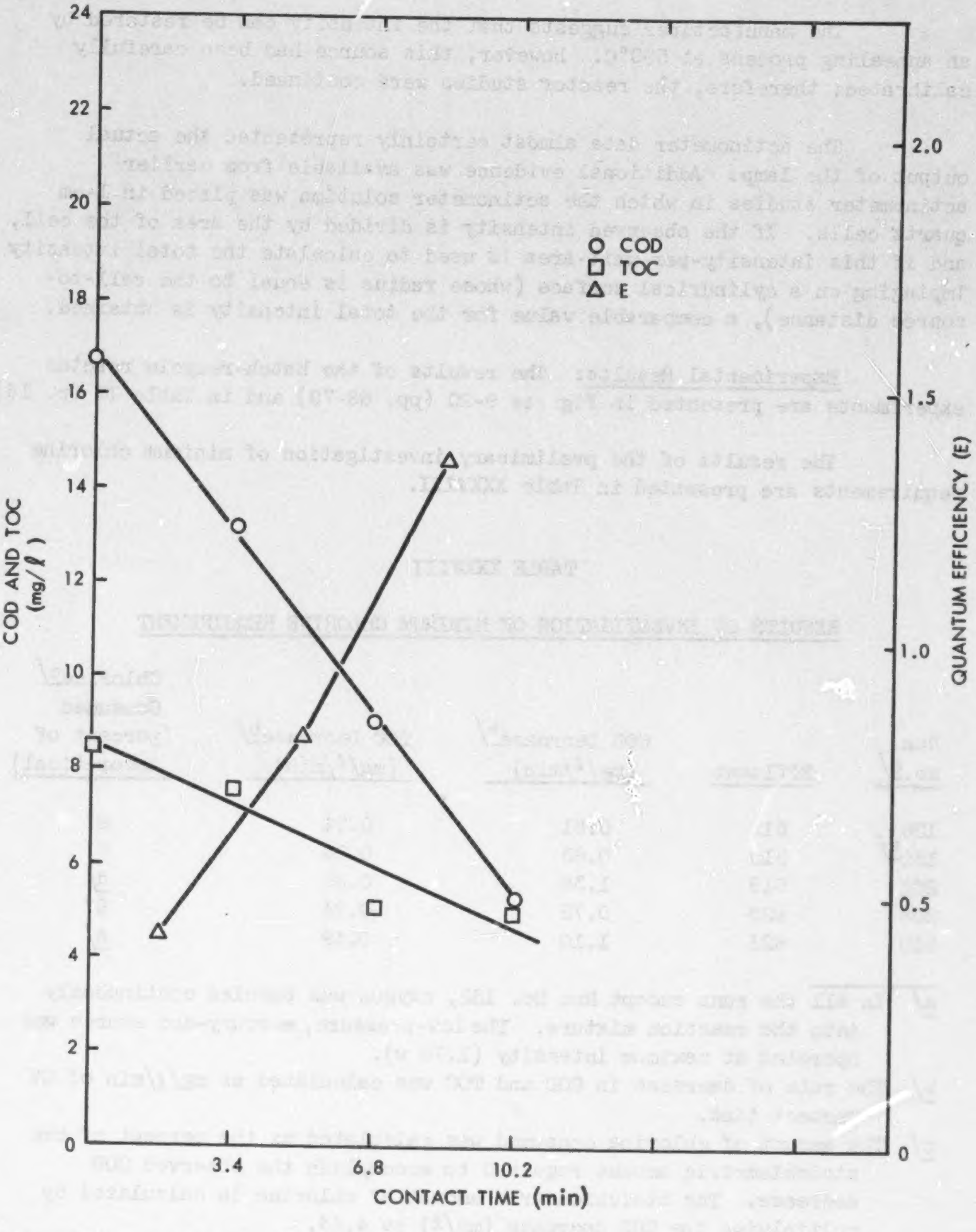

Figure 9 - Batch-Recycle Reactor Results - High Intensity - High Flow Rate (Effluent MRI 112, Run No. 66)

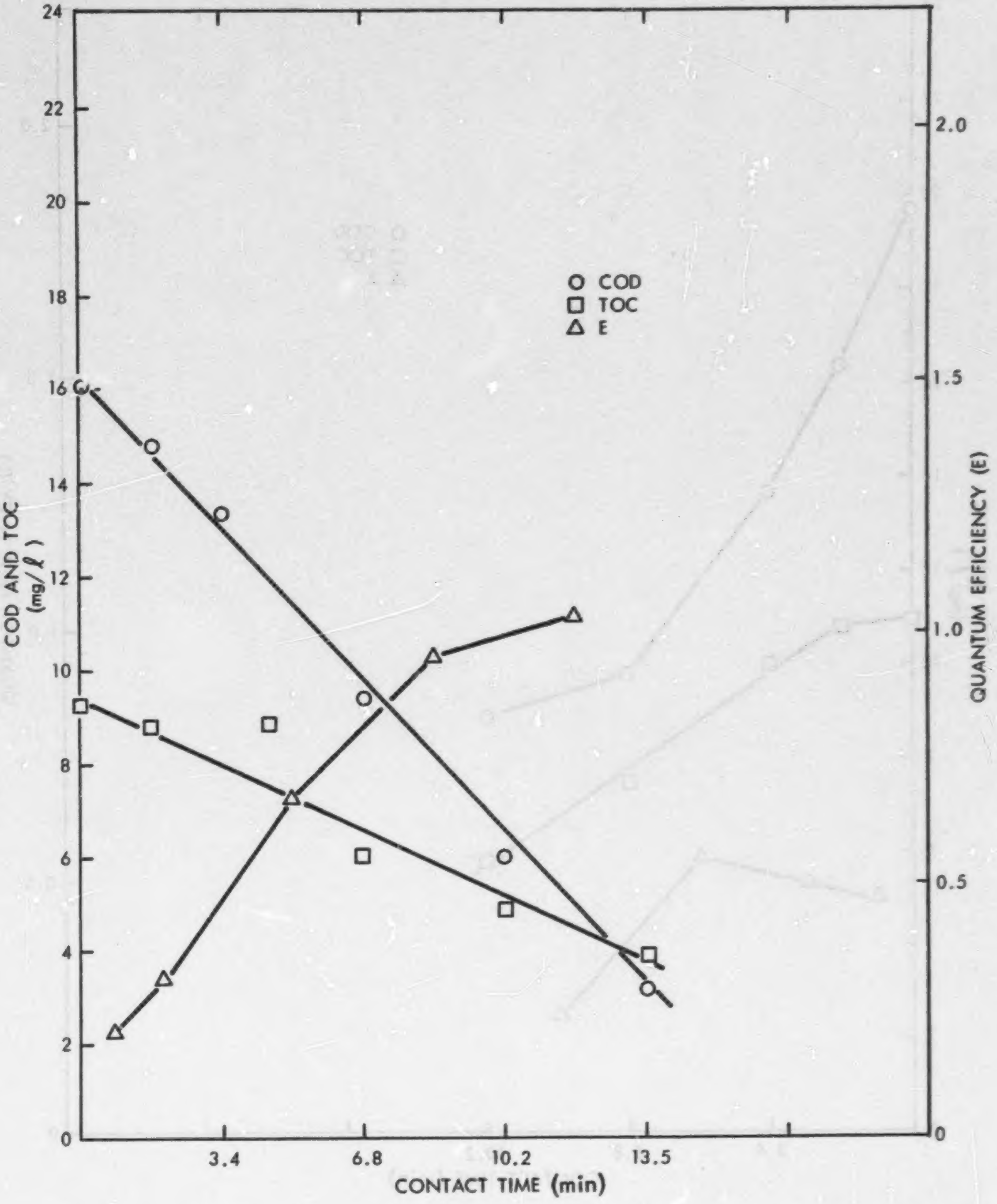

Figure 10 - Batch-Recycle Reactor Results - High Intensity - High Flow Rate (Effluent MRI 112, Run No. 68)

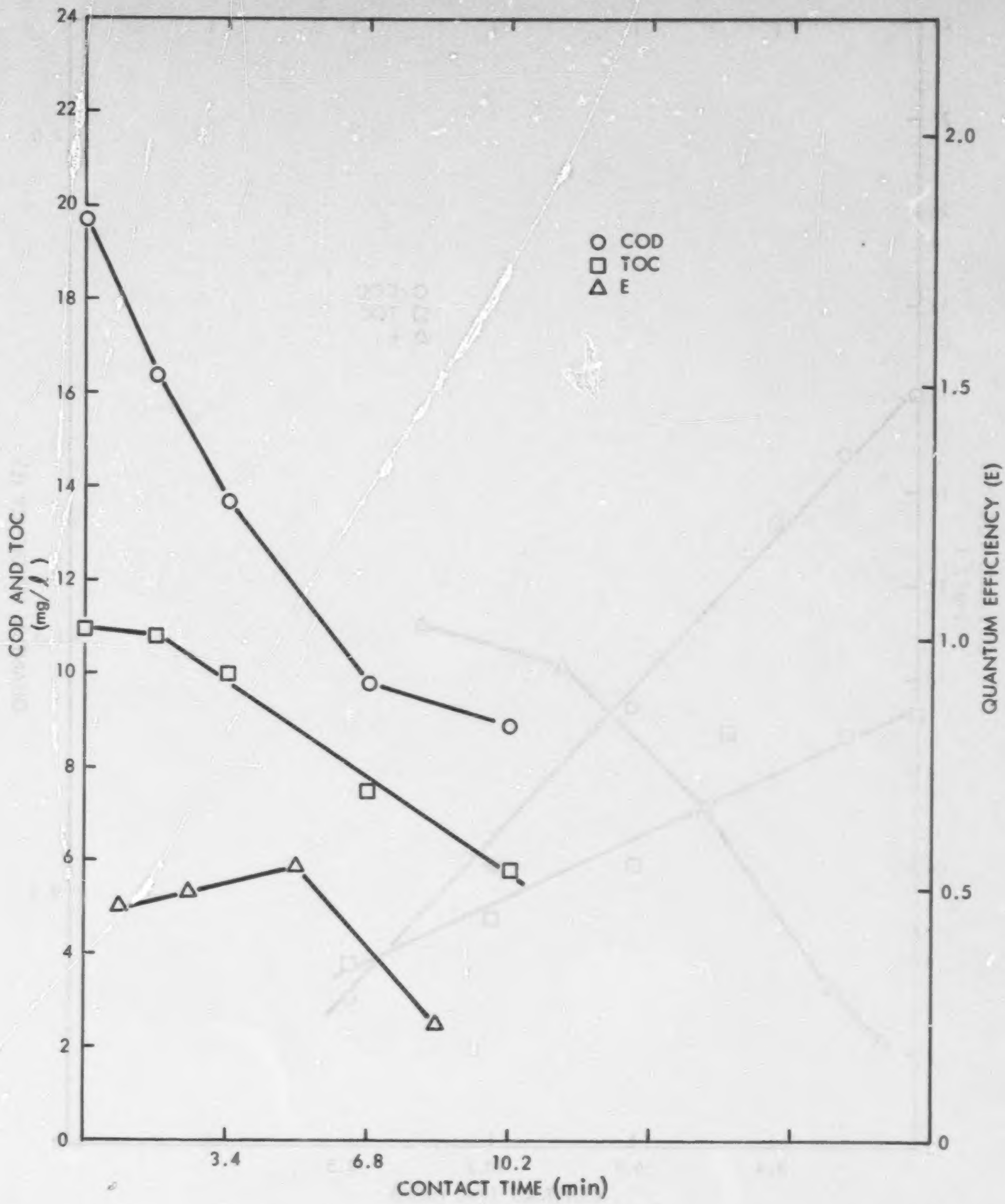

Figure 11 - Batch-Recycle Reactor Results - High Intensity - High Flow Rate (Effluent MRI 304, Run No. 74)

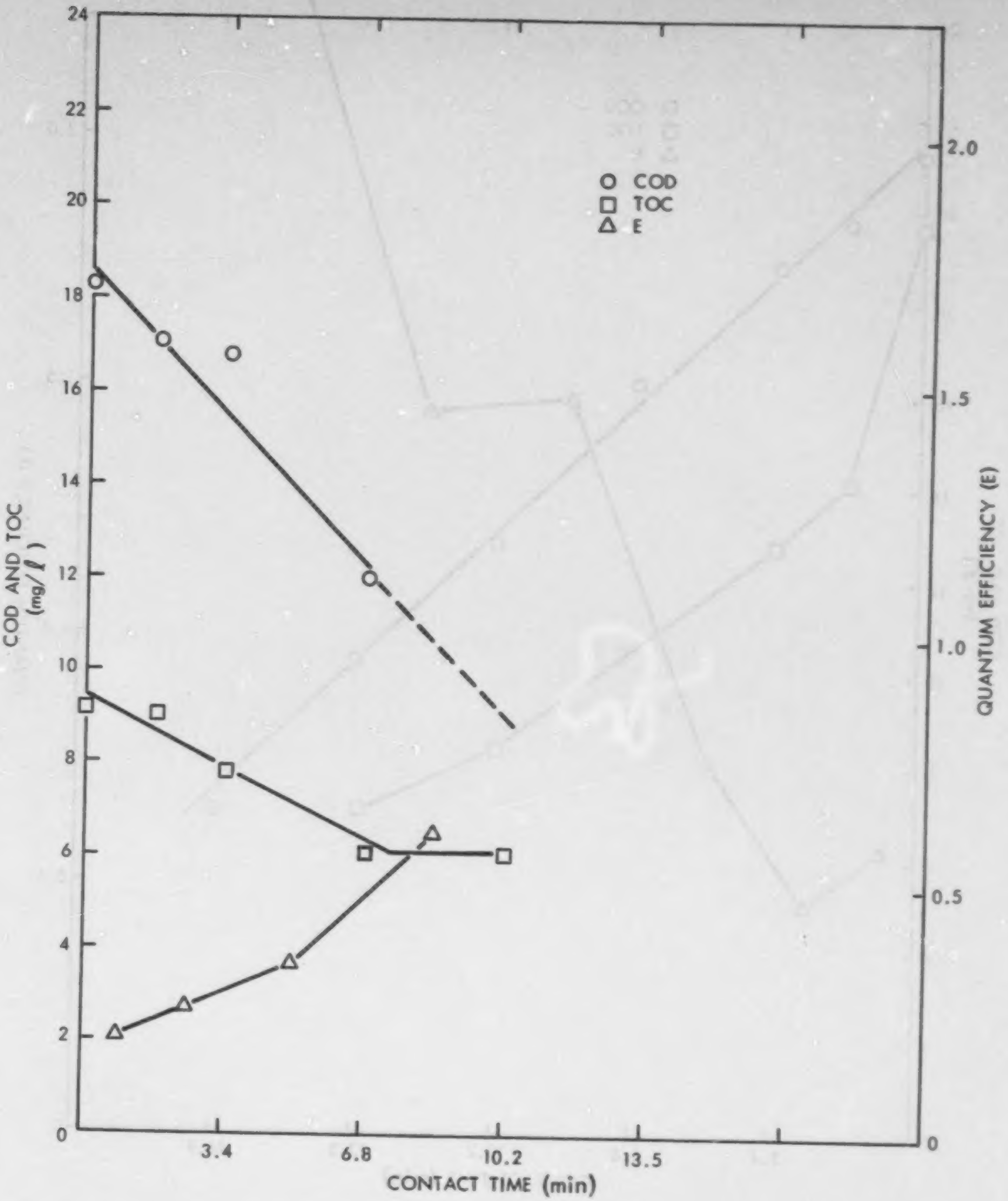

Figure 12 - Batch-Recycle Reactor Results - High Intensity - Low Flow Rate (Effluent MRI 304, Run No. 78)

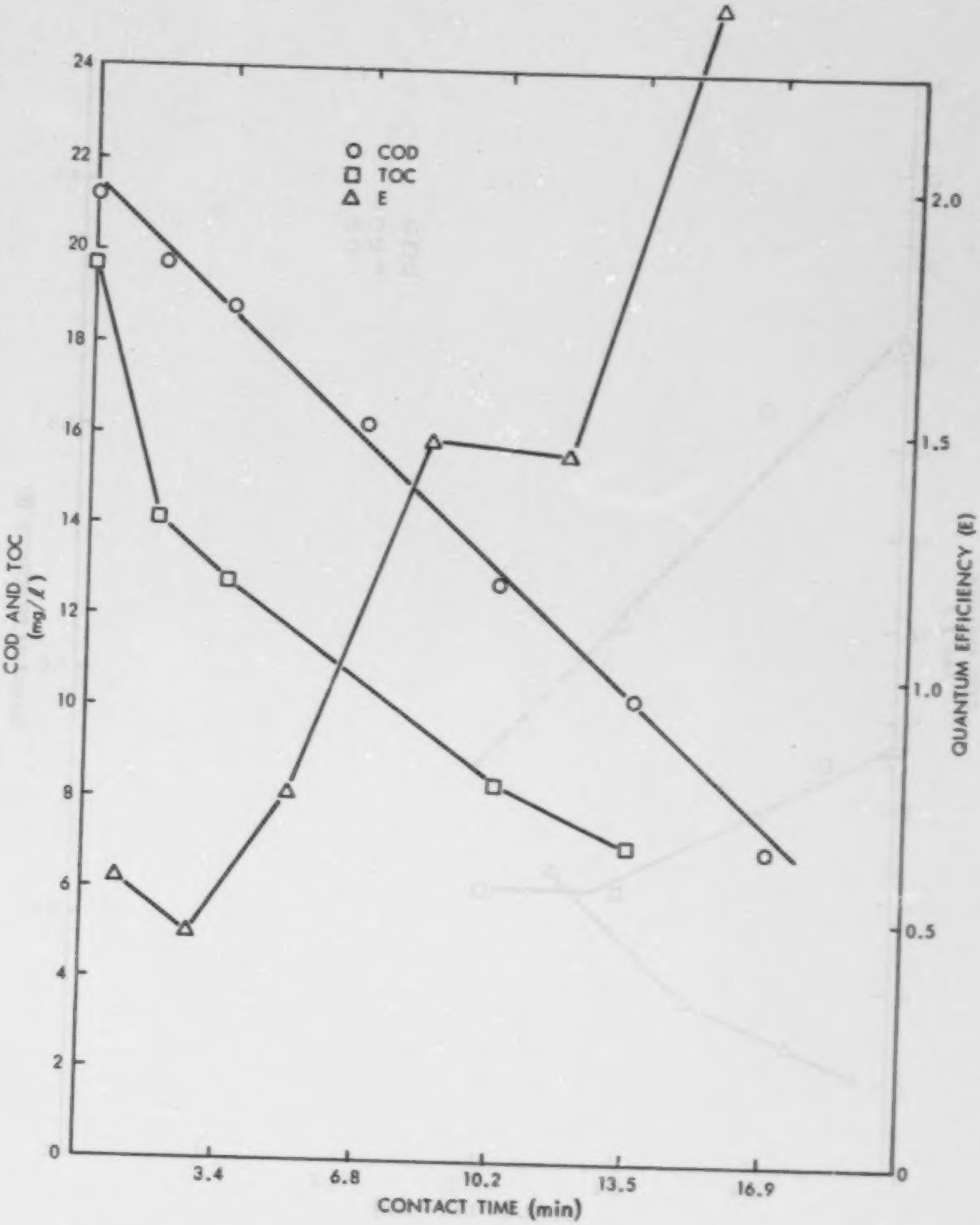

Figure 13 - Batch-Recycle Reactor Results - Low Intensity - High Flow Rate (Effluent MRI 304, Run No. 82)

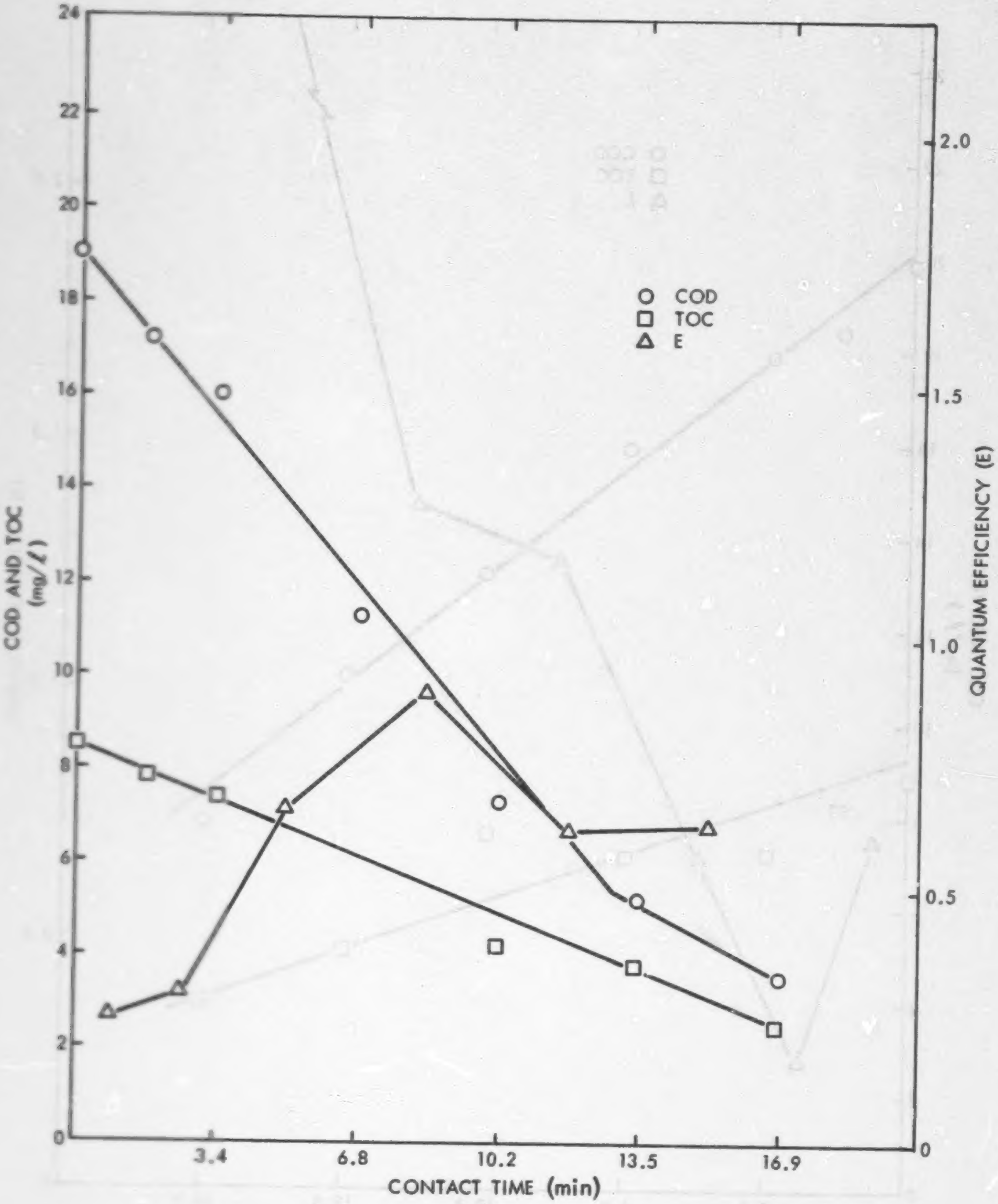

Figure 14 - Batch-Recycle Reactor Results - High Intensity - High Flow Rate (Effluent MRI 310, Run No. 86)

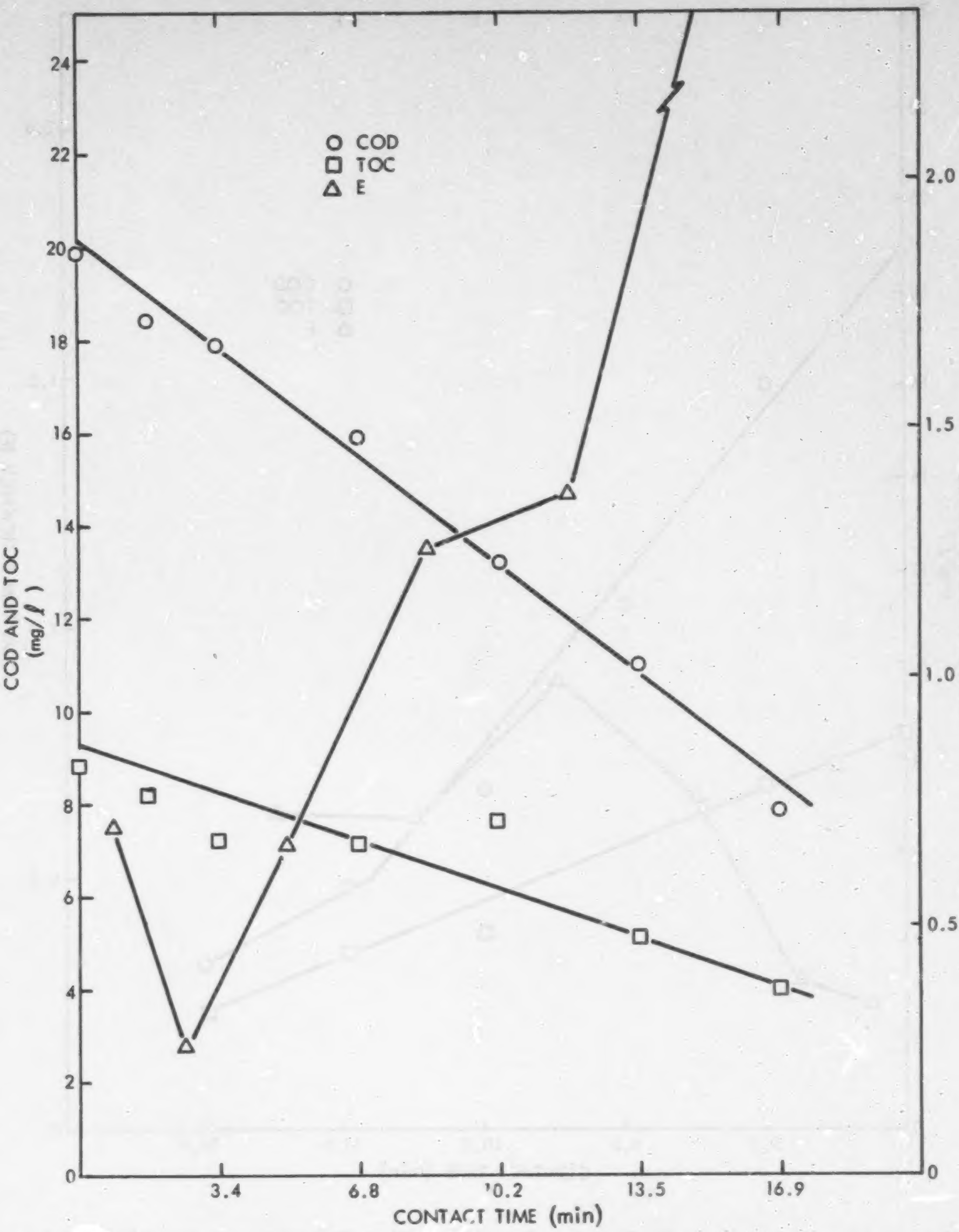

Figure 15 - Batch-Recycle Reactor Results - Low Intensity - High Flow Rate (Effluent MRI 310, Run No. 93)

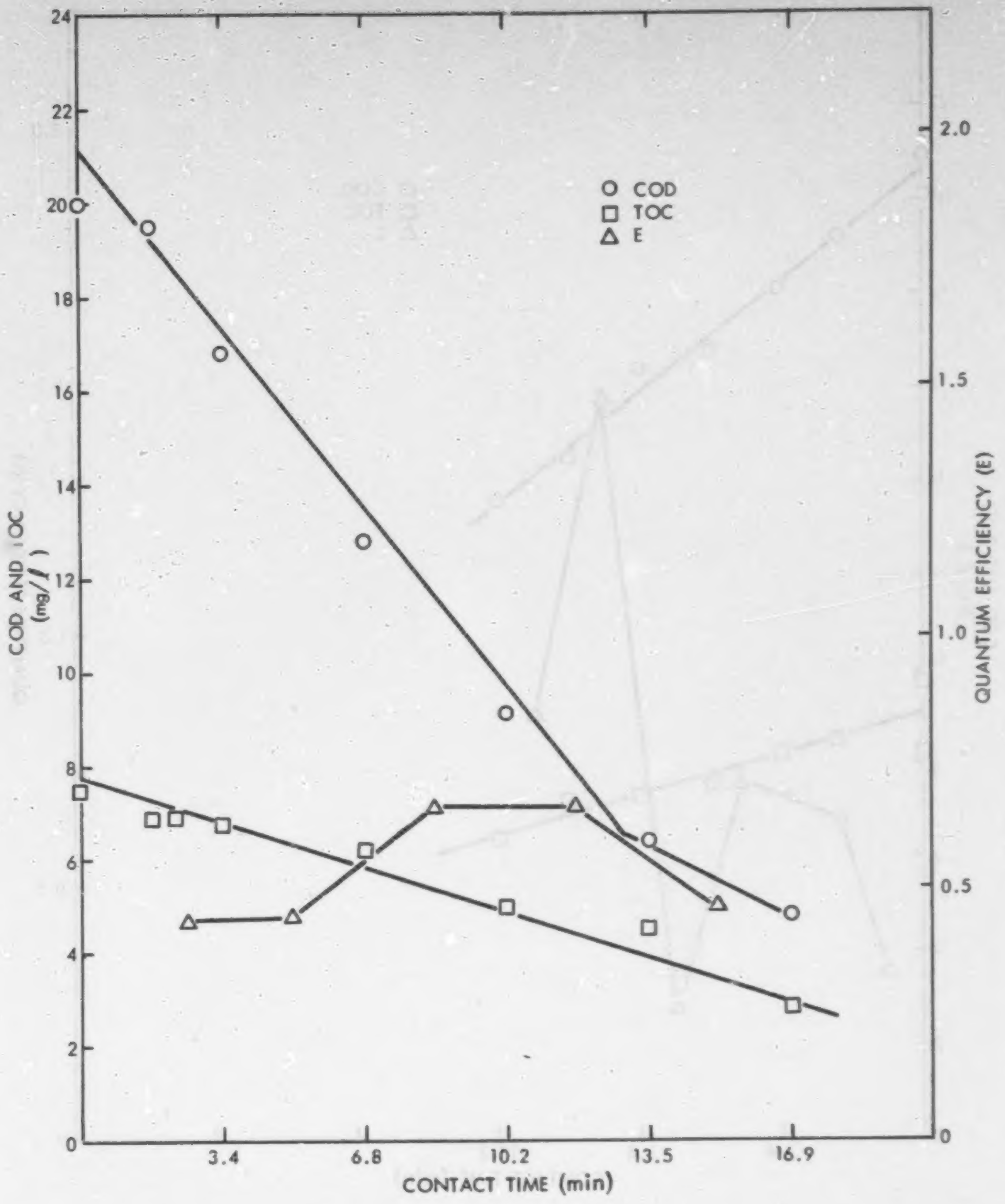

Figure 16 - Batch-Recycle Reactor Results - High Intensity - Low Flow Rate (Effluent MRI 310, Run No. 101)

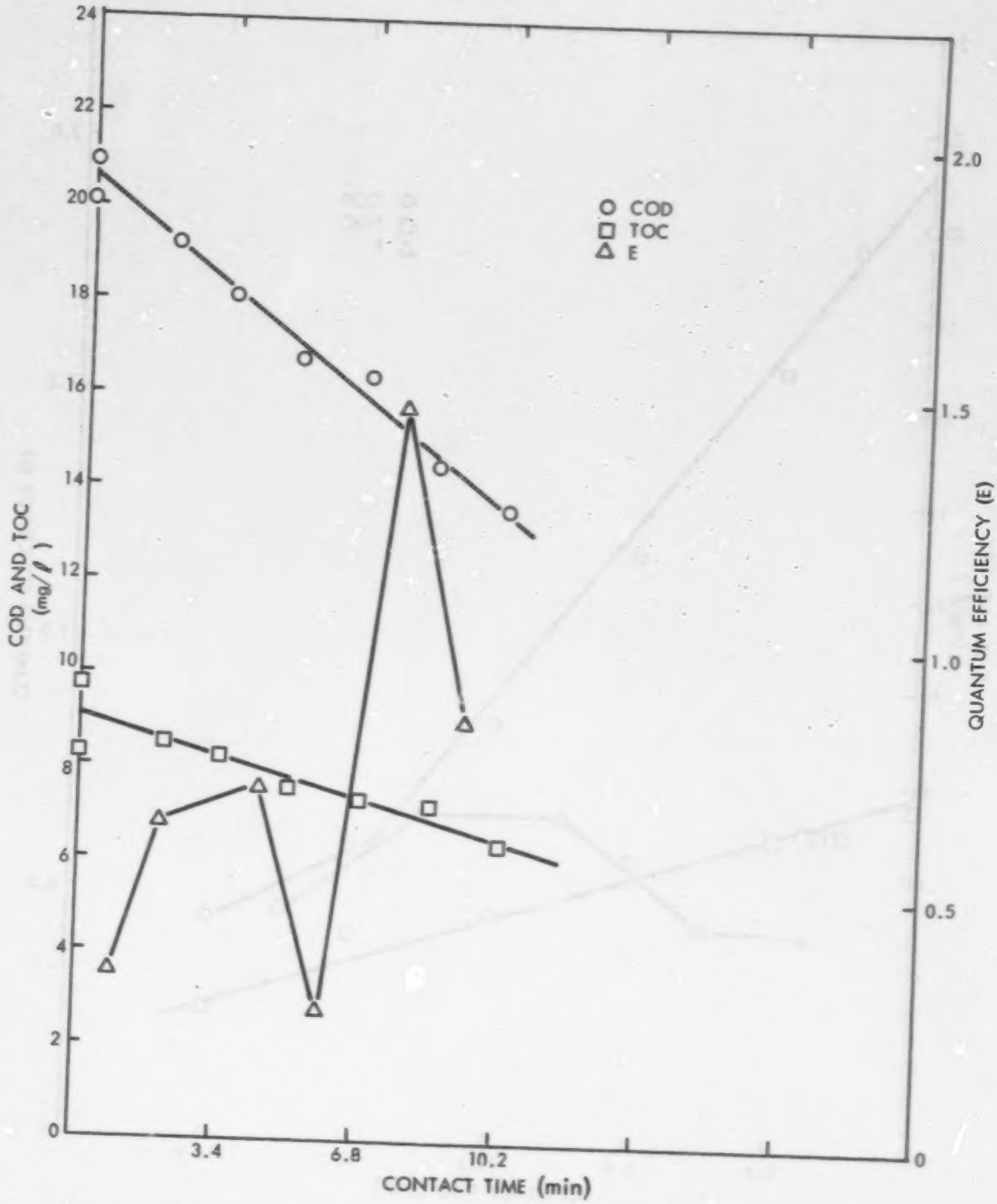

Figure 17 - Batch-Recycle Reactor Results - Low Intensity - High Flow Rate (Effluent MRI 319, Run No. 104)

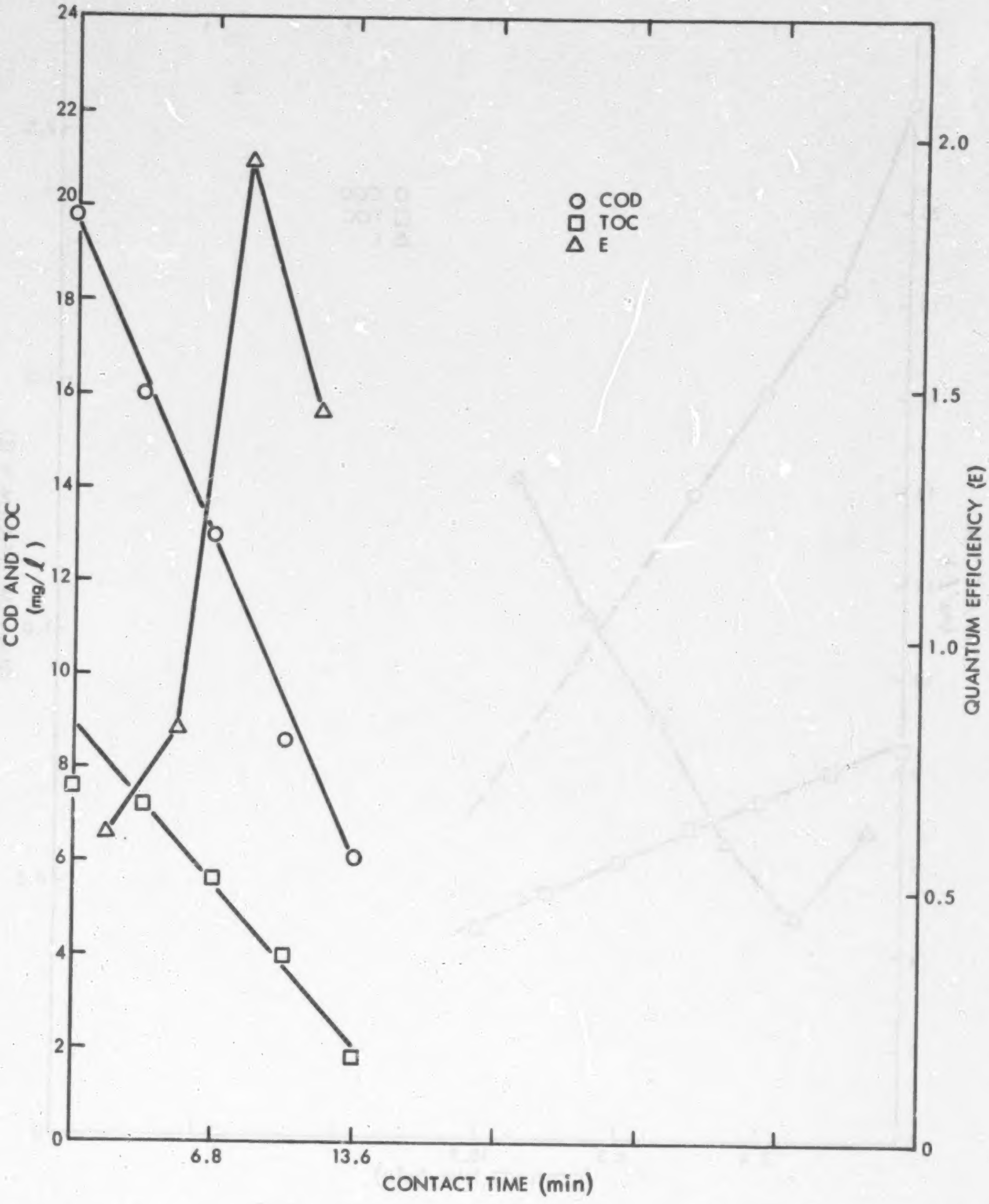

Figure 18 - Batch-Recycle Reactor Results - High Intensity - High Flow Rate (Effluent MRI 319, Decreased Volume, Run No. 108)

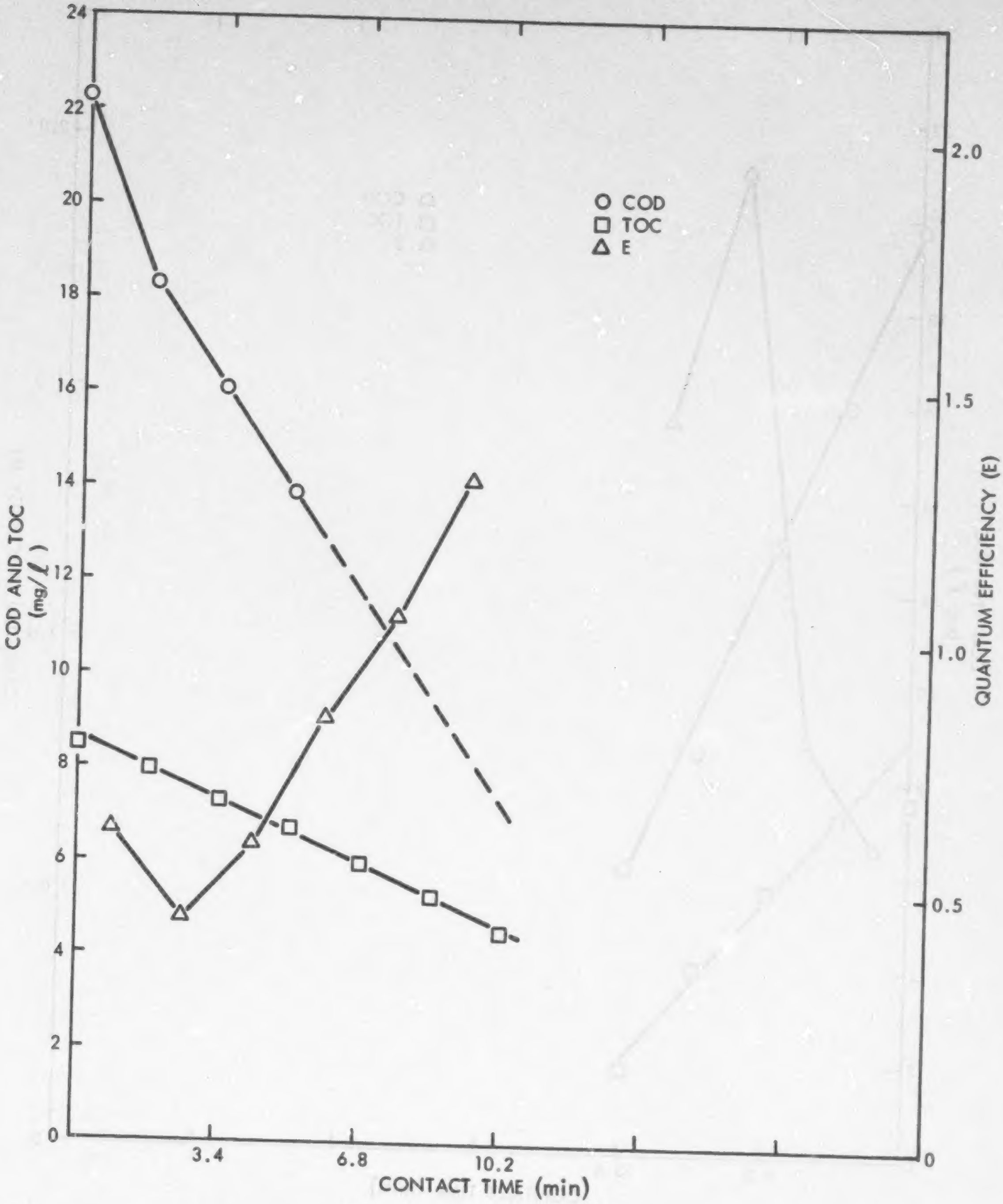

Figure 19 - Batch-Recycle Reactor Results - High Intensity - High Flow Rate (Effluent MRI 319, Run No. 112)

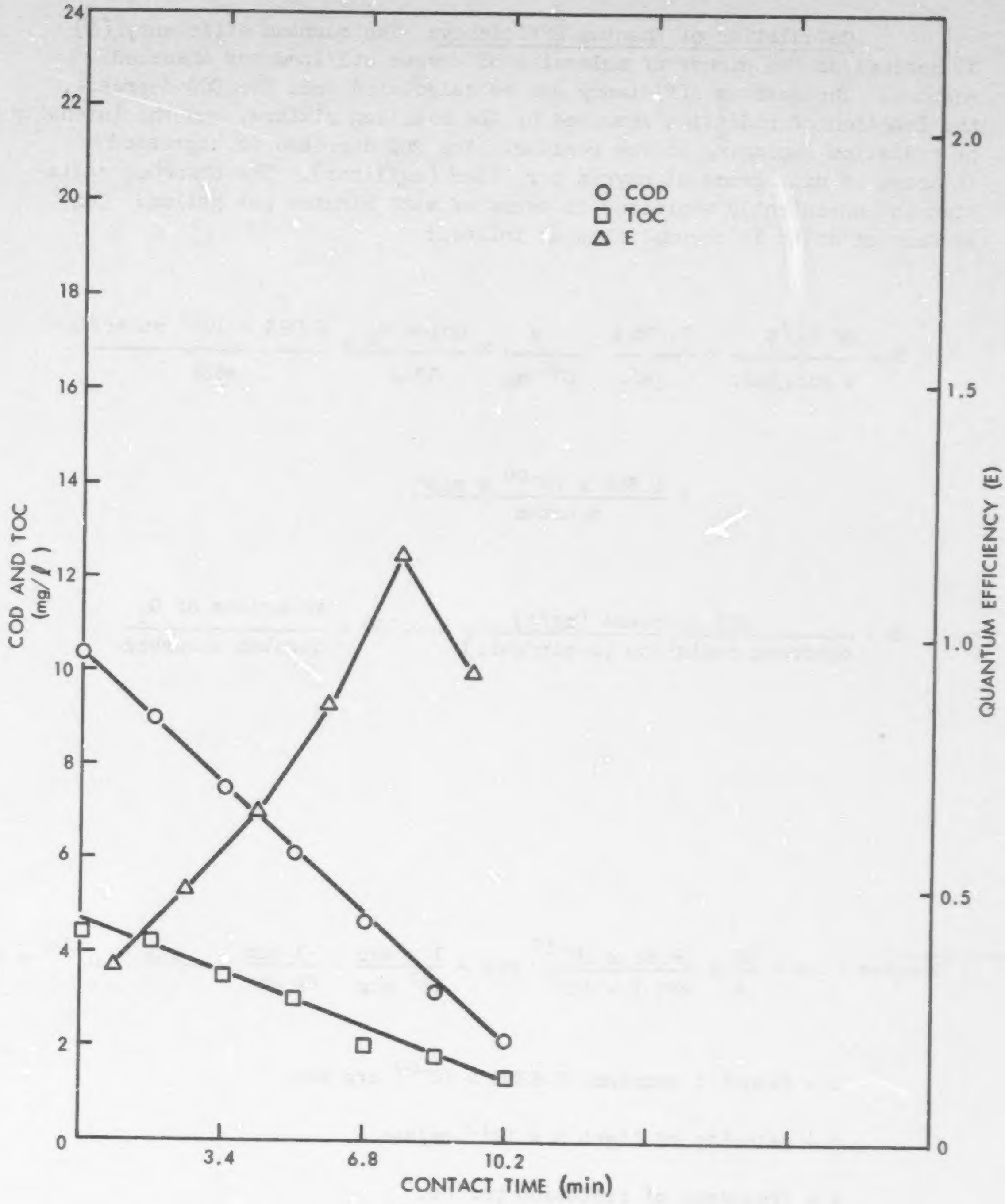

Figure 20 - Batch-Recycle Reactor Results - High Intensity - High Flow Rate (Effluent MRI 319, Diluted, Run No. 117)

Calculation of Quantum Efficiency: The quantum efficiency (E) is defined as the number of molecules of oxygen utilized per absorbed quantum. The quantum efficiency can be calculated from the COD decrease, the fraction of radiation absorbed by the reaction mixture, and the intensity of radiation impinging on the reactor. The COD decrease is expressed in terms of milligrams of oxygen per liter (mg/liter). The absorbed radiation is conveniently expressed in terms of watt minutes per gallon. Conversion of units is accomplished as follows:

$$E = \frac{\text{mg } O_2/\ell}{\text{w min/gal.}} \times \frac{3.785\ \ell}{\text{gal.}} \times \frac{\text{g}}{10^3 \text{ mg}} \times \frac{\text{moles } O_2}{32 \text{ g}} \times \frac{6.023 \times 10^{23} \text{ molecules}}{\text{mole}}$$

$$\times \frac{1.305 \times 10^{-20} \text{ w min}^*}{\text{quantum}}$$

$$E = \frac{\text{COD decrease (mg/}\ell)}{\text{absorbed radiation (w min/gal.)}} \times 0.930 = \frac{\text{molecules of } O_2}{\text{quantum absorbed}}$$

$$* \quad 1 \text{ Quantum} = h\nu = \frac{hc}{\lambda} = \frac{19.86 \times 10^{-17}}{253.7 \times 10^{-7}} \text{ erg} \times \frac{1 \text{ w sec}}{10^7 \text{ erg}} \times \frac{1 \text{ min}}{60 \text{ sec}} = 1.305 \times 10^{-20} \text{ w min}$$

h = Planck's constant 6.6255×10^{-27} erg sec

c = velocity of light 3×10^{10} cm/sec

ν = frequency of radiation per sec

λ = wavelength in cm

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The project was conducted under the general supervision of Dr. C. C. Chappelow, Jr., Head, Organic and Polymer Chemistry at MRI.

The Project Officer for the Water Quality Office, Environmental Protection Agency, was Mr. Robert H. Wise.

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APPENDIX A

PROBLEMS REGARDING SOURCE SELECTION FOR LARGE-SCALE, LIGHT-CATALYZED, CHLORINE OXIDATION

In order to determine which radiant-energy source is best suited to the catalytic oxidation process, it is simply necessary to determine which source produces the greatest amount of oxidation for the least cost. However, selection of the best radiant-energy source cannot be made easily by a trial-and-error basis because there are so many possible sources.

Adequate information is available concerning the relative amounts of each wavelength emitted by radiation sources which are presently available. The large-volume costs of these sources can also be readily estimated. The problem then is to determine which wavelengths are most capable of catalyzing the oxidation.

The usefulness of a given wavelength will depend upon three factors: (1) the relative catalytic effectiveness of the wavelength compared to other wavelengths; (2) the ability of the selected wavelength to penetrate wastewater; and (3) the cost of producing that wavelength compared to other wavelengths.

The first two factors can be determined experimentally, and the third factor must be considered in relation to the various sources available; the ideal source will be the one which produces the greatest amount of the most useful wavelengths for the least cost.

Many types of radiation sources are commercially available. Certain modifications of existing sources are also possible which alter the wavelength output and useful life of the sources. A somewhat over-simplified statement of this situation is that shorter lifetimes and higher radiant-energy costs are encountered if shorter wavelengths or higher intensities are required.

A thorough review of all potential radiation sources is beyond the scope of this report. Louis R. Koller in his text entitled Ultraviolet Radiation[1] has provided an excellent review of the various sources of radiant energy. He devotes 68 pages to the discussion of electrical arcs and 16 pages to a discussion of incandescent sources. Since incandescent sources are relatively weak and inefficient sources of ultraviolet radiation, we have given consideration only to the electrical arcs.

The most efficient and most useful sources of ultraviolet energy are the arcs. Arcs are produced when a current of electricity is passed between electrodes separated by a gas or a vapor. The amount of ultraviolet radiation available depends upon the nature of the arc.

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[1] Koller, L. R., Ultraviolet Radiation, 2nd Edition, John Wiley & Sons, Inc., New York (1965).

There are two main types of arcs: open arcs and closed arcs. The carbon arc is a typical example of an open arc, and it produces radiant energy with the arc exposed to the atmosphere. In closed arcs, of which mercury-vapor lamps are typical examples, electrical discharges through a gas or vapor are contained in an envelope which is usually of quartz or glass. Arcs may take place through any desired gas or vapor and at pressures ranging from a few microns up to hundreds of atmospheres. The pressure is limited only by the strength of the envelope. The gases and vapors include such diverse substances as hydrogen, helium, argon, neon, krypton, xenon, mercury, cadmium, zinc, tellurium, and magnesium.

The spectrum of most arcs is chiefly due to the discharge through the gas or vapor and so is usually of the line or band type. In high-pressure arcs there is also a continuous background over a part of the spectrum. In some cases, such as the carbon arcs, the incandescent electrodes may also contribute a continuous component to the spectrum, so that line and continuous spectra may be present in various proportions.

Mercury Arcs

Mercury arcs have been used extensively for the generation of ultraviolet radiation. There are several reasons for the choice of mercury: (1) its spectrum is rich in lines of the ultraviolet; (2) it is fairly inert and does not react with electrode materials; (3) it does not attack glass appreciably; and (4) its vapor pressure lies in a convenient range for lamps which operate near room temperature.

A wide variety of mercury arcs is available commercially. They differ from each other in such respects as operating pressure, bulb shape, reflector, electrodes, starting mechanisms and other features which suit them to perform specific tasks. Literally hundreds of different kinds have been developed. The spectral energy distributions of selected mercury-arc lamps are shown in Table A-I.

Essentially, mercury arcs are characterized by the mercury vapor pressure. This parameter of pressure is an important one in determining the wavelengths and intensity of radiation generated by the discharge.

High-Pressure Mercury Arcs: High-pressure mercury arcs have proved to be useful sources of ultraviolet, as well as of visible, radiation. They emit intense bands of ultraviolet radiation between 220 mμ and 366 mμ. One of the fundamental characteristics of high-pressure arcs is the high temperature of the gas and the thermal equilibrium between the gas and the electrons. The temperatures range from 5500° to 8000°F. High-pressure arcs require much greater energy input per unit length than low-pressure arcs.

TABLE A-I

SPECTRAL ENERGY DISTRIBUTION (IN W)
OF SELECTED, MERCURY-ARC LAMPS[a]

Type of Mercury Arc	G.E. Ordering Abbreviation	Far UV (220-280 mμ)		Middle UV (280-320 mμ)		Near UV (320-400 mμ)		Visible (400-700 mμ)	
High-pressure	UV-37	252	(22%)	279	(25%)	252	(22%)	347	(31%)
Medium-pressure	H1500-A23	189	(26%)	157	(22%)	140	(20%)	227	(32%)
Low-pressure	G64T6	18.0	(90%)	0.4	(2%)	0.3	(1.5%)	1.3	(6.5%)
Floodlamp	H400-A34-1	0	(0%)	1.5	(2%)	20.5	(26%)	55.7	(72%)
Sunlamp	RS	0.004	(0%)	1.4	(12%)	3.1	(27%)	7.0	(61%)
"Black light" Fluorescent	F40BL	0	(0%)	0.33	(3%)	7.3	(72%)	2.6	(25%)

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[a] These data were obtained from several sources provided by the General Electric Company.

They are characterized by a very brilliant, small-diameter arc operating at a relatively large current density and high voltage. High-pressure arcs are shorter than low-pressure arcs of the same voltage and also have a smaller tube diameter. Compared to other mercury arcs, high-pressure mercury arcs have relatively short, lamp-lifetimes (1,000 hr).

Low-Pressure Mercury Arcs: As the vapor pressure of mercury in a discharge is reduced, the intensity of the 253.7-mμ line (known as the mercury resonance line) increases markedly. This phenomenon is exploited in the construction of low-pressure lamps which emit this radiation almost exclusively.

Lamps of this kind are widely used for germicidal purposes because they are the cheapest sources of sterilizing radiation. Maximum germicidal effect is produced by wavelengths near 260 mμ, and germicidal effectiveness drops off sharply at lower and at higher wavelengths; wavelengths above 320 mμ are almost completely ineffective for germicidal purposes.

Low-pressure mercury arcs emit much-less-intense radiation than high-pressure mercury arcs of about the same physical dimensions. However, the useful life of low-pressure lamps is much longer (7,500 hr). Also, low-pressure lamps are considerably less expensive than high-pressure lamps of the same ultraviolet-energy output. Low-pressure lamps also convert electrical energy to radiant energy more efficiently.

Sunlamps: Ultraviolet lamps which are used for therapy are known as sunlamps. The term sunlamp, however, has a very specific meaning and cannot be applied to ultraviolet lamps indiscriminately. The Council of Physical Therapy of the American Medical Association defines a sunlamp as a lamp that, at a specified distance, emits ultraviolet radiation not differing essentially with that of natural sunlight in total intensity. Its spectral range must extend from about 290 mμ to and including 313 mμ. Wavelengths shorter than 280 mμ are undesirable.

Since all mercury-vapor arcs emit considerable radiation of shorter wavelength than 280 mμ, it is necessary to filter out this radiation in order to make them conform to the above definition. This can be done by filtering the light from an intermediate-pressure, quartz, mercury lamp using a glass which does not transmit radiation below 280 mμ. Another alternative is to make the lamp envelope of a filter material.

"Black Light" Fluorescent Lamps: Low-pressure mercury arcs are used to produce ultraviolet in the region around 366 mμ, popularly known as "black light." "Black light" is very effective in exciting fluorescence in many substances. The inside wall of a "black light" lamp is coated with a phosphor which absorbs the 253.7-mμ radiation and emits in a broad band around 366 mμ. Thus, the phosphor transforms 253.7 mμ radiation into longer-wavelength ultraviolet. The glass used in constructing the tube does not transmit the short-wavelength ultraviolet but allows the longer wavelengths to pass through. The phosphor commonly used is a cerium-activated calcium phosphate.

The output of ultraviolet energy between 320 mμ and 380 mμ is a greater percentage of the electrical input for these lamps than for any other kind of mercury discharge. The percent of visible radiation is greater than that for germicidal lamps, but is less than that for any of the sunlamps. Consequently, "black light" fluorescent lamps are very useful for producing fluorescent effects, blue printing and other applications. They emit practically no radiation of wavelengths shorter than 320 mμ.

High-Pressure, Mercury-Arc Floodlamps: Special types of high-pressure, mercury-arc lamps have been developed for illumination purposes. Lamps of this kind are characterized by a very brilliant, small-diameter arc operating at a relatively large current density and high voltage. These lamps are often called "Capillary Type Lamps" since they are constructed of small diameter, heavy-walled, quartz tubes. These tubes are usually enclosed in an outer jacket of glass which serves a threefold purpose of filter, heat insulator, and shield in case of breakage of the arc tube. Lamps of this kind are widely used for illumination purposes and are therefore relatively cheap compared to other types of mercury-arc lamps which are not used in such large quantities. Because of the nature of their use, exceptionally long operating lifetimes are required. Lamps of this kind are available which have lifetimes of 24,000 hr, and greater. Also as would be expected, most of the radiation (70 to 75%) from these lamps is in the visible region. However, because of their relatively long life and low cost, lamps of this kind are relatively inexpensive sources of ultraviolet radiation.

A comparison of the costs of producing ultraviolet radiation from various types of mercury-arc lamps is presented in Table A-II.

TABLE A-II

COSTS OF PRODUCING ULTRAVIOLET RADIATION FROM VARIOUS MERCURY-ARC LAMPS[a]

Lamp (G.E. Ordering Abbreviation)	Type[b]	Lamp Cost[c] ($)	Daily Cost[d] ($)	Daily Cost of 100 w of UV Output ($)
UA-37	HP	147.00	3.68	0.470
G64T6	LP	14.00	0.0448	0.242
H1500-A23	MP	112.50	0.450	0.0927
H400-A33-1	FL	12.40	0.0124	0.0564
F40BL	BL	2.00	0.004	0.0888
RS	SL	9.00	0.108	2.40

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[a] The data in this table were obtained from General Electric.

[b] HP = High pressure, LP = Low pressure, MP = Medium pressure, FL = Floodlamp, BL = "Black light," SL = Sunlamp.

[c] These figures are the large-scale replacement costs of the individual lamps.

[d] The daily cost is the replacement cost, divided by the lamp life in days.

Carbon Arcs

The carbon arc is a typical example of an open arc. It consists of a discharge between two carbon electrodes in air at atmospheric pressure. The arc is started by bringing the two electrodes into contact and then separating them slightly. The resulting discharge is intensely bright and hot.

During operation, the electrodes are consumed. The positive electrode is burned at the rate of about 2 in/hr in low-intensity arcs and as much as 12 in/hr in high-intensity arcs. The negative electrode is consumed at a somewhat slower rate. In order to maintain the constancy of the arc, the electrode must be fed (either by hand or by an automatic device) in order to maintain a constant arc-gap.

The spectrum of the carbon arc consists of the continuous spectrum of the incandescent electrodes on which is superimposed the band spectrum of the luminous gas. The resulting spectrum is relatively continuous. The cyanogen bands between 380 mμ and 390 mμ are a particularly marked feature of this spectrum and add a pronounced peak in this region.

This peak is very noticeable in Figure A-1 which depicts the spectral energy distribution of a typical carbon arc.

Increased ultraviolet output can be produced from carbon arcs by the addition of certain substances, such as iron, to the carbon core. Figure A-2 shows the spectral energy distribution of a carbon arc with iron-cored carbons. This spectrum has many lines ranging from the visible through the ultraviolet to 230 mμ. The overall ultraviolet output is considerably greater than that produced by ordinary carbon arcs, although the output of visible radiation is considerably less.

The spectral outputs that can be obtained, using carbon arcs of different compositions, are shown in Table A-III. Compared to mercury arcs, carbon arcs are very intense, though not necessarily efficient, sources of ultraviolet. Their usefulness is based on the fact they are extremely concentrated sources; that is, a larger amount of radiation can be produced from a smaller area of radiating surface. However, if efficiency is an important consideration, the carbon arcs are less efficient in many cases than mercury arcs. For example, the intensity of radiation between 230 mμ and 280 mμ at a distance of 1 m from a National W carbon Arc is 1970 $\mu w/cm^2$. Since the input to the arc is 4800 w, the "yield" of radiant energy is 0.41 $\mu w/cm^2/w$ input. The intensity in the same wavelength range and at the same distance from a 30-w germicidal lamp is 75 $\mu w/cm^2$, or 2.5 $\mu w/cm^2/w$ input.

In general, the advantages lie with the carbon arc if a high intensity is required from a single unit. On the other hand, when efficiency is a consideration, the advantage usually lies with the mercury arc.

The relatively short life of a carbon arc (namely, a few hours before the carbons must be replaced) is a disadvantage in comparison with the life of an enclosed arc (namely, several thousand hours). However, devices are available which can automatically feed carbon rods to an arc on a 24-hr basis. In some applications, the presence of the combustion products of the arc is also a disadvantage.

High-Pressure Xenon Arcs

Until about 1950, mercury-vapor arcs were the most widely used arcs both in therapy and in industry. Since then, there has been a notable increase in the use of high-pressure xenon arcs, particularly for industrial and technological applications.

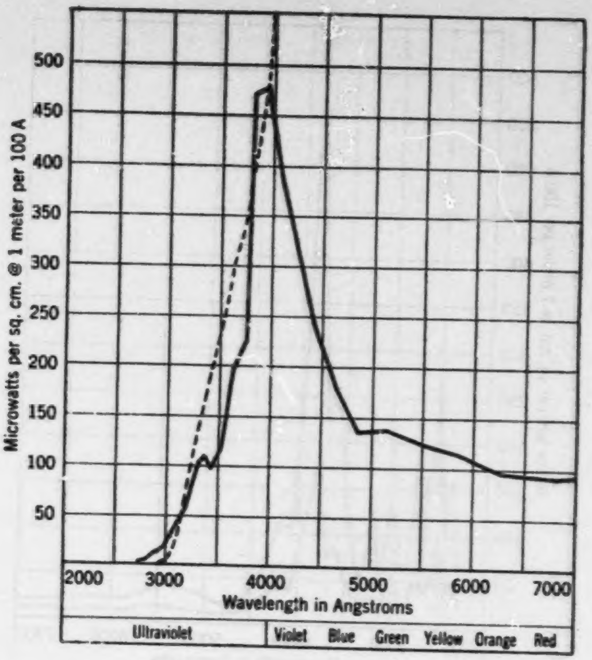

Figure A-1 - National Sunshine Carbon, with Corex D Filter, Compared with Natural Sunlight. Solid line, with Corex D filter; dotted line, natural sunlight.

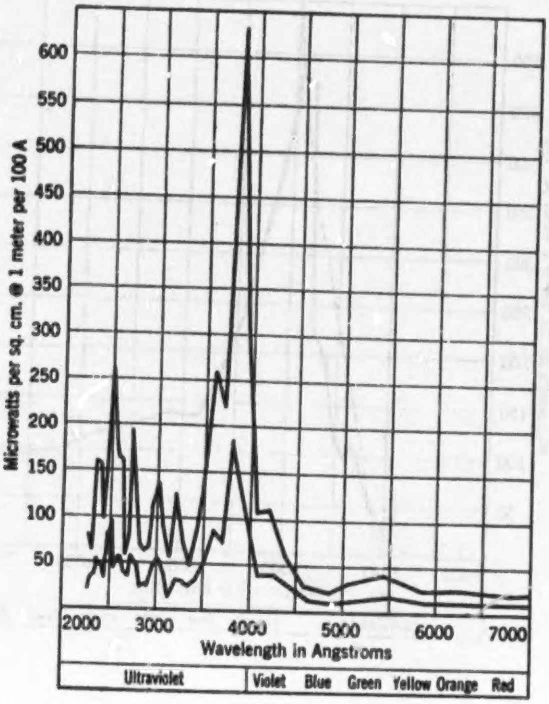

Figure A-2 - Spectral Energy Distribution of Carbon Arc With Iron-Cored Carbons (National B). Upper curve, 60-amp alternating current, 50 v across arc. Lower curve, 30-amp alternating current, 50 v across arc.

TABLE A-III

INTENSITY OF RADIATION FROM BARE CARBON ARCS, WITHOUT REFLECTORS, IN MICROWATTS PER SQUARE CENTIMETER AT DISTANCE OF 1 METER FROM ARC*

Type of Arc	Current	Volts	2300-2800 Å	2800-3800 Å	3200-3800 Å	2300-3800 Å	3800-7000 Å
"National" Sunshine carbon	60	50	129	187	1010	1326	6094
"National" Sunshine carbon with Corex D filter	60	50	2	103	860	965	5445
"National" B carbon	60	50	684	326	1010	2020	1910
"National" C carbon	60	50	613	413	1188	2214	1656
"National" D carbon	60	50	80	40	296	416	1819
"National" E carbon	60	50	221	130	584	935	5665
"National" K carbon	60	50	709	262	1310	2281	1529
"National" U carbon	60	50	746	589	1000	2335	2148
"National" W carbon	80	60	1970	1627	2620	6217	6223

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* Calculated from National Carbon Company Catalog, Section A-4300.

Xenon arcs, between tungsten electrodes operating at pressures in the 10- to 30-atm range, are efficient sources of intense visible and ultraviolet radiation. At these pressures, the xenon spectrum becomes a continuum extending from the ultraviolet into the visible and then the infrared. Commercial xenon lamps range in size from 150 to 20,000 w. A typical spectrum of this type of lamp is shown in Figure A-3. The spectrum varies somewhat with input to the lamp and with the operating pressure; however, the general character is not affected. The brightness of these lamps is comparable to that of the carbon arcs.

Xenon arcs are presently replacing carbon arcs in certain applications, particularly lithographic processes. The cost of xenon arcs is usually four to five times the cost of comparable carbon arcs. However, because of their convenience, and especially because of their cleanliness, lithographers are in the process of converting to these types of lamps. It should be mentioned, however, that the cost of illumination in lithographic processes represents a very small fraction of the overall operating costs.

General Considerations in Arc Selection

The choice of an arc for a particular application depends upon several factors. Foremost is the wavelength of the desired radiation. Other factors are the presence of absence of other wavelengths, plus total yield, efficiency and intensity of the source. The total yield depends upon the kind of lamp and the wattage. For a given type, the total yield may sometimes be increased by employing a higher wattage. The yield, however, is quite distinct from the efficiency. The efficiency depends upon the kind of lamp; thus the efficiency of production of 253.7-mμ radiation is about 24% for a 30-w, low-pressure, germicidal lamp; while it is 3% for a high-pressure, mercury-arc lamp. In spite of the higher efficiency, the total output of 253.7-mμ radiation from the germicidal lamp is only one-fourth as great as from the high-pressure lamp. The radiant flux, per unit area, produced by the germicidal lamp is the lowest of any of the mercury-arc sources. Extremely high radiant flux, per unit area, is produced by high-pressure, mercury-arc lamps because of their relatively small dimensions.

The germicidal lamp emits very little radiation other than the 253.7-mμ radiation. However, the high-pressure mercury lamp is a rich source of longer-wave ultraviolet, visible and infrared radiation. High-pressure xenon arcs, which have practically a continuous spectrum, radiate only about 9% of their energy in the region below 400 mμ.

The selection of the ideal, radiant-energy source depends upon many factors. Where small, compact sources are required, high-pressure lamps or carbon arcs are favored. Where efficiency is a consideration in order to avoid unnecessary heat loads, other types of lamps are required.

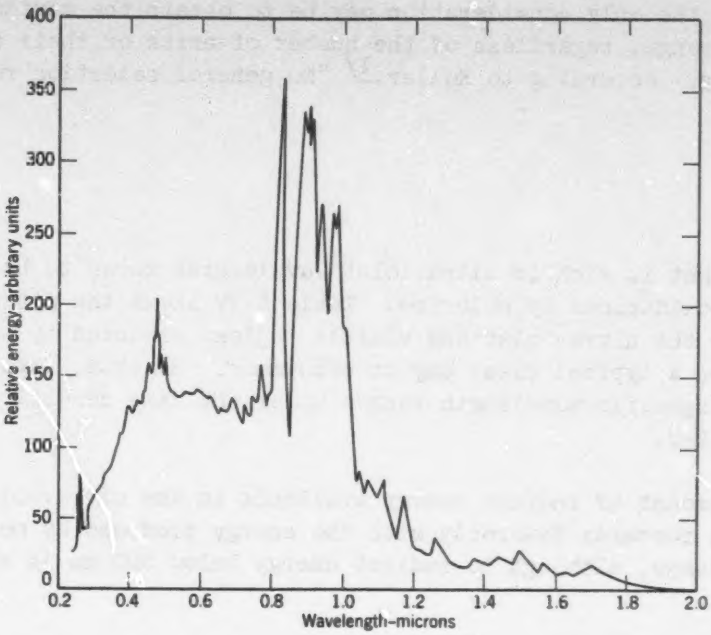

Figure A-3 - Spectral Energy Distribution of Typical 5-KW Xenon Lamp. Electrode radiation excluded.

In other cases, the only consideration may be to obtain the maximum output in the desired range, regardless of the number of units or their size or their efficiency. According to Koller,[1] "No general selection rules can be given."

Sunlight

Sunlight is rich in ultraviolet wavelengths known to be useful for catalyzing oxidations by chlorine. Table A-IV shows the intensity of illumination in the ultraviolet and visible regions produced by sunlight during midday on a typical clear day in midsummer. Maximum, total, radiant energy, within specific wavelength ranges under the same conditions, is shown in Table A-V.

The amount of radiant energy available in the ultraviolet and visible regions compares favorably with the energy produced by mercury-arc or carbon-arc lamps, although no radiant energy below 300 mμ is available from sunlight.

Although obviously the cheapest source of radiant energy, sunlight presents the troublesome problem of periodic, as well as random, fluctuations in occurrence and intensity. However, even if use of sunlight were technically feasible, standby sources of radiation would probably be required to prevent unusually large accumulations of untreated or partially treated wastewater during periods of greatly decreased illumination.

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[1] Koller, L. R., Ultraviolet Radiation, 2nd Edition, John Wiley & Sons, Inc., New York (1965).

TABLE A-IV

SOLAR ENERGY DISTRIBUTION*

Wavelength (mμ)	Intensity of Illumination* $(\mu w/cm^2)$
300	5.2
310	47.5
320	125
330	204
340	233
355	259
370	325
385	333
400	433
410	548
420	600
430	617
440	627
450	669
500	718
550	689
600	621
650	556
700	549

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* Intensities are calculated assuming a horizontal surface during midday on a typical clear day in midsummer in Cleveland, Ohio; latitude 41.5°N. Intensities are calculated for each spectral band of 5 mμ centered at the various wavelengths. From "Germicidal, Erythemal and Infrared Energy," by M. Luckiesh, D. Van Nostrand Company, New York, 1946, p. 48.

TABLE A-V

MAXIMUM INTENSITY OF SOLAR ENERGY*

Wavelength Range	Radiant Energy $(\mu w/cm^2)$
Shorter than 350 mμ	1,180
350-400 mμ	2,360
400-700 mμ	42,000
Longer than 700 mμ	40,800
TOTAL	86,340

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* Intensities are calculated assuming a horizontal surface during midday on a typical clear day in midsummer in Cleveland, Ohio; latitude 41.5°N. From "Germicidal, Erythemal and Infrared Energy," M. Luckiesh, D. Van Nostrand Company, New York, 1946, p. 35.

APPENDIX B

SELECTION OF TECHNIQUES AND EQUIPMENT FOR WAVELENGTH-EFFECT STUDIES

Prior to the wavelength-effect studies, there were a number of alternatives to consider in the selection of the monochromatic radiation source, the design of the reaction vessel and the method of determining the amount of radiation absorbed. These alternatives are discussed below.

Selection of Monochromatic Radiation Source: There are two general methods for providing monochromatic, or nearly monochromatic, radiation for studies of this kind. The most direct procedure is to employ a monochrometer. A monochrometer is an instrument which separates individual wavelengths, being emitted by polychromatic sources, by means of a prism or grating. All ultraviolet spectrophotometers are equipped with monochrometers; however, these monochromatic sources are far too feeble to be of practical value in photochemistry. Monochrometers which produce fairly intense monochromatic radiation are commercially available; however, these are very expensive and are not common laboratory equipment. Most photochemical data involving the use of a monochrometer have been supplied by investigators who have constructed their own monochrometer. The major problem is to produce a monochromatic source of sufficiently high intensity. Another problem is that the rectangularly shaped image of the slit produces a radiation beam which is not compatible with the reaction vessel and is not homogeneous in intensity.

Another method for producing nearly monochromatic radiation is to use filters. There are three principal types of filters: chemical filters, glass filters, and interference filters. Chemical filters are simply solutions of certain chemical compounds of known spectral transmission. Many filters of this kind have been used for various photochemical applications.

Glass filters are the most familiar type of optical filter, and glass filters are available which will cleanly separate any desired visible wavelength from a medium-pressure mercury arc. Unfortunately, no such series of glass filters have been developed for the ultraviolet region.

Interference filters consist of two, semitransparent, evaporated metal films on glass plates which are separated by a transparent layer of a thickness comparable to a particular, desired wavelength of light. The filter reflects all incident light except for that characteristic band.

Interference filters provide several advantages over other types of filters. Besides allowing a relatively short, optical path between source and reactor cell, interference filters do not become warm during use because practically all of the radiation which is not transmitted is reflected. Interference filters are stable at elevated temperatures (108°F), and they cannot fade or change their transmission properties since the nature of their filtering action does not depend on light absorption.

A major factor in the ultimate decision concerning experimental techniques employed in the wavelength-effect studies was the very recent availability of interference filters for the ultraviolet region. A series of interference filters was obtained which permitted very effective isolation of the major wavelengths available in a high-pressure mercury arc.

An interference filter capable of isolating the important line of mercury-arc radiation at 253.7 mμ was not readily available. To produce monochromatic radiation of this wavelength, a low-pressure mercury arc was employed. Data supplied by the manufacturer of this lamp (Nester/Faust) indicate that 96% of the UV output of this lamp is in the range, 245 to 260 mμ, with a characteristically sharp maximum at 253.7 mμ.

Photochemical Reactor Cells: The most common and functional design of reactor cells for quantitative liquid-phase studies is a cylindrical cell with optically flat, circular windows fused to the cell body at right angles to its axis. The size of the cylinder and windows should be consistent with the dimensions of the light beam used in the experiments. There should be as little unradiated cell volume as possible, so that there can be no question about the actual effective volume of the cell.

In quantitative photochemical work it is desirable to use flat windows and to have nearly perpendicular incidence of the light beam on the window. Under these conditions, the fraction of light reflected at the window interface is a minimum. If a curved surface, such as the wall of a test tube or flask, is placed in a homogeneous light beam, much of the incident radiation will be lost, and the distribution of light within the vessel will be very nonhomogeneous.

For our purposes, the most convenient, photochemical reactor cells were the quartz, cylindrically shaped cells used to hold samples for ultraviolet spectrum determinations. Cells of this kind have flat, perpendicular, quartz windows, and cells of 1, 5, and 10 cm in length were readily available. The diameter of these cells is about 2 cm, a size which permitted uniform irradiation of the cell by the radiation transmitted by the interference filters. A further convenience of these cells results from the fact that the ultraviolet spectrum of the substance could be determined before and after the experiment. These spectral data were required in order to determine the amount of radiation absorbed by the chlorinated effluent; the data were also useful in determining the extent of organic oxidation and in determining the effective depth of penetration of various wavelengths.

Actinometry: In order to compare the effect of radiation at one wavelength with the effect of radiation of another wavelength, it is necessary to know the intensity of the radiation at both wavelengths. In the wavelength-effect studies, it was necessary to determine accurately the intensity of the radiant energy impinging upon the photochemical reactor. In general, intensity is detected by physical or chemical methods. Devices which employ physical methods include thermopiles, bolometers, radiometers, phototubes, photoconductive cells, and photovoltaic cells. The advantages and disadvantages of these detectors are discussed in considerable detail by Koller.1/

In our opinion, actinometry (the determination of the intensity of radiant energy by chemical methods) was the best method for solving this particular problem.

An actinometer is a radiation-measuring, chemical device which consists of chemicals that undergo a visible, or easily measurable, change on exposure to radiation. There exists a very useful and accurate actinometer which is based upon the rate of photochemical decomposition of oxalic acid in the presence of uranyl sulfate. The amount of oxalic acid decomposed is determined by titration with permanganate.2/

A more sensitive actinometer is based on the photolysis of ferrioxalate. This method depends upon the photometric determination of the photolysis products.3/ It is hundreds of times more sensitive than the uranyl-oxalate method. The minimum detectable energy is 3×10^{14} quanta. This method can be used to investigate weak sources without making unduly long exposures. The quantum yield is of the order of unity at all wavelengths up to 510 mμ.

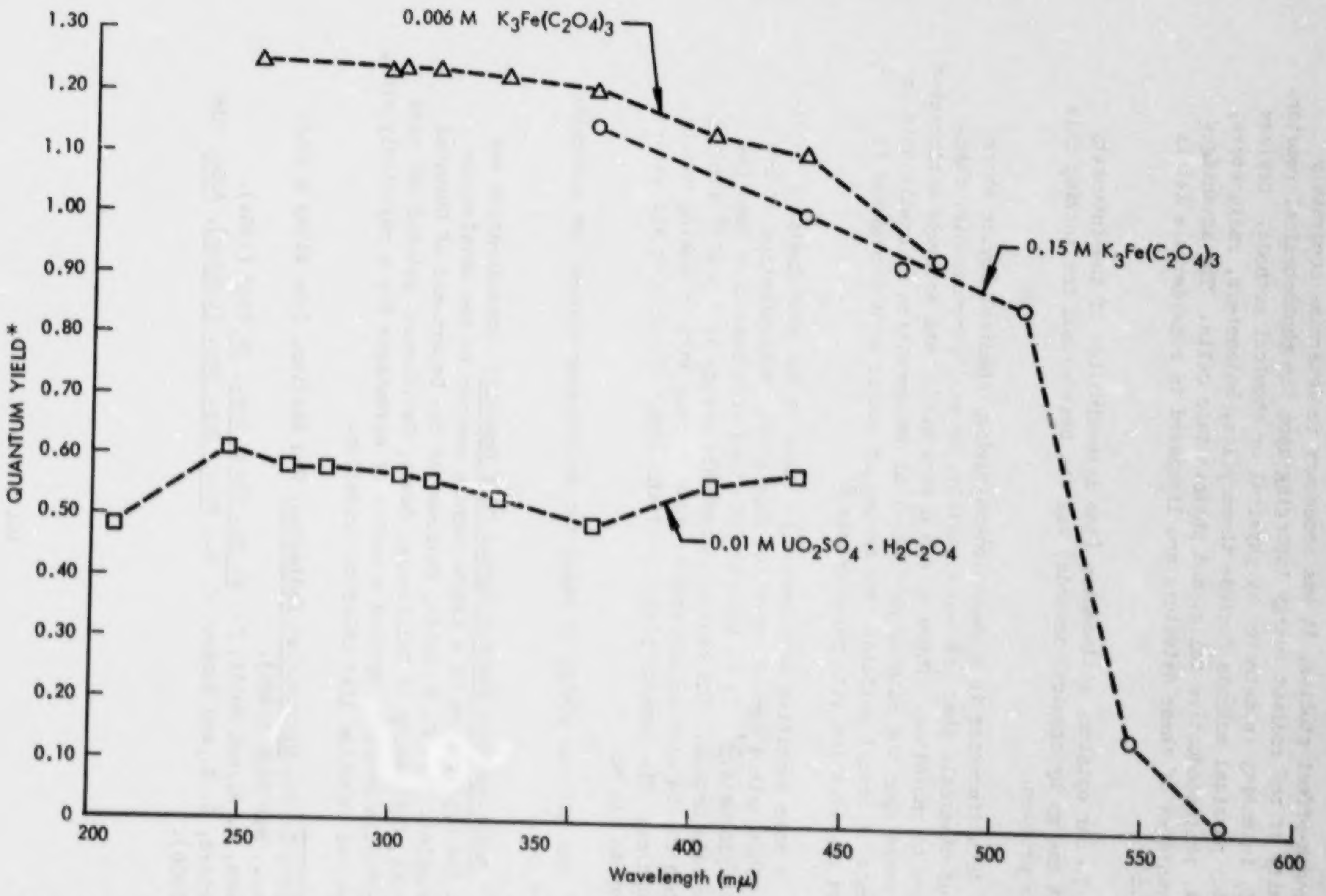
The quantum yields of these two actinometer systems are presented in Figure B-1.

Batch-Recycle Reactor Versus Cell Reactor: Consideration was given to the application of a batch-recycle reactor to the wavelength-effect studies. Dr. J. M. Smith, Chairman of the Department of Chemical Engineering, University of California, Davis, California, pointed out that a batch-recycle reactor provided a number of advantages for a relatively slow, photochemical reaction like chlorine oxidation.

1/ Koller, L. R., Ultraviolet Radiation, 2nd Edition, John Wiley & Sons, Inc., New York (1965).

2/ Forbes, G. S., and Heidt, L., J. Am. Chem. Soc., 56, 2363 (1934).

3/ Hatchard, C. G., and Parker, C. A., Proc. Roy. Soc. (London), A235, 518 (1956).



* Quantum yield = $\frac{\text{No. of molecules of product formed/cm}^3\text{-sec}}{\text{No. of quanta absorbed/cm}^3\text{-sec}}$. For $K_3Fe(C_2O_4)_3$, the product is ferrous ion; for $UO_2SO_4 \cdot H_2C_2O_4$, the product is CO_2, the amount of which is expressed in terms of oxalate ion lost.

Figure B-1 - Quantum Yields of Chemical Actinometers

Essentially, a batch-recycle reactor of the type used by Dr. Smith is a vertical quartz tube through which the reaction mixture flows. The mixture is pumped from a reservoir through the irradiated, quartz-tube reactor and is returned to the reservoir. The reactor tube is located at one focus of an elliptical reflector system, and the radiation source is located at the other focus of the system. A series of concentric filters are located around the radiation source to permit variation in the wavelength and intensity of the radiant energy.

In the batch-recycle reactor system, the optical purity of the incident radiation is far from monochromatic, but the loss of monochromatic character is offset by the increased intensity of the available radiation.

The procedure of using a batch (i.e., nonrecycle) reactor, such as the photochemical reactor cell, for relatively long periods of time (in order to produce detectable changes in concentration) can cause inaccuracies because of the lack of mixing. In the absence of mixing there are uncertainties because of temperature and concentration gradients. However, according to Dr. Smith, no method has been developed for mixing in a photochemical batch reactor without influencing the radiation path. Since earlier studies[4/] had shown (1) that the UV-chlorine oxidation is not affected by temperature and (2) that the rate of oxidation is not proportional to chlorine concentration, it was felt that the lack of mixing would not be a serious problem.

Another disadvantage of the small reactor cell is that the pH must be controlled by means of buffers, not by the intermittent addition of sodium hydroxide, as the reaction proceeds. Therefore, it was necessary to perform experiments in a large reactor in order to demonstrate that there was no significant difference between the results obtained with buffers and the results obtained by maintaining pH by alkali addition.

A further disadvantage in using a system in which interference filters are employed to provide monochromatic radiation is the small volume of reaction mixture employed. Because the size of the reaction vessel is limited to a cell about 1 in. in diameter and 1 to 5 cm in depth, determinations of chemical oxygen demand (COD) were not possible because of the small volumes of samples available.

Because of the small size of a cell reactor, chlorine cannot be added gradually and the required amount of chlorine must be added at the

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[4/] "An Investigation of Light-Catalyzed Chlorine Oxidation for Treatment of Wastewater," Final Summary Report, FWPCA Contract No. 14-12-72, December 1968.

beginning of the experiment. High chlorine concentrations were necessary because relatively large decreases in TOC were required for precise determinations of changes in organic concentration. However, high chlorine concentrations were not considered to be a major problem because the original work on UV-chlorine oxidation had shown that chlorine concentration did not affect the rate of TOC or COD decrease.

Thus, it was felt that reliable data concerning the effect of wavelength could be obtained using the cell reactor in spite of the necessity for relatively high chlorine concentrations.

In summary, there are advantages and disadvantages to both types of reactor systems, and these are summarized below:

Batch-Recycle Reactor

Advantages

1. Permits large volumes of reaction mixture; thus, COD as well as TOC determinations can be performed.
2. Permits pH control by alkali addition.
3. Avoids problems of unmixed reactor.
4. More like ultimate reactor system.
5. Can utilize relatively intense radiation at reactor area.

Disadvantages

1. Cannot utilize monochromatic radiation.
2. Actinometer results are only approximate.
3. Reactor is relatively elaborate to construct.

Cell Reactor

Advantages

1. Can utilize truly monochromatic radiation.
2. Can use actinometer precisely.

Disadvantages

1. Buffers must be used for pH control.
2. Small volume of reactor precludes COD determinations.

3. Can obtain quantitative wavelength effects.	3. Cannot be stirred since that might cause temperature and concentration gradients.
4. Is relatively simple to operate (using interference filters).	4. Incident radiation is relatively feeble; therefore, long reaction times may be required.

The final decision was to construct a cell reactor for the wavelength-effect studies and to employ a batch-recycle reactor to obtain other reactor-design factors.

1 Accession Number	2 Subject Field & Group 05D	**SELECTED WATER RESOURCES ABSTRACTS** **INPUT TRANSACTION FORM**

5 **Organization**

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425 Volker Boulevard
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6 **Title**

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10 **Author(s)**

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16 **Project Designation**

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22 **Citation**

Contractor's Final Report

23 **Descriptors (Starred First)**

Aerobic Treatment, Environmental Engineering, Oxygen Demand, Oxygen Requirements, Pollution Abatement, Waste Assimilative Capacity, Water Pollution Control, Chlorination*, Ultraviolet Light Catalysis*, Secondary Effluent Treatment*

25 **Identifiers (Starred First)**

Chlorine, Light Catalysis

27 **Abstract**

Application of light-catalyzed chlorine oxidation to the treatment of effluents from secondary waste-treatment plants was studied. Wavelength effects, intensity-time relationships, quantum efficiencies, chlorine concentration and the effect of dissolved oxygen were studied in both a small batch reactor and a large batch-recycle reactor.

For optimum organic oxidation rate, optimum utilization of radiant energy and most efficient use of chlorine, (1) low intensity, short-wavelength radiation should be employed, and (2) the chlorine concentration should be at a minimum (less than 5 mg/liter).

A plant for processing 10 million gallons of effluent per day was designed. Estimated costs for construction and operation of this plant totaled 11.77¢/1,000 gal. Results to date indicate that raw materials costs (chlorine and caustic) can be reduced, and that actual quantum efficiencies will be higher than the conservative efficiency upon which this estimate is based.

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